Fluctuating-bias controlled electron transport in molecular junctions

Michael Ridley,[1,2] Angus MacKinnon,[2] and Lev Kantorovich[1]
[1]*Department of Physics, King's College London, Strand, London, WC2R 2LS, United Kingdom*
[2]*Department of Physics, The Blackett Laboratory, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom*
(Received 9 February 2016; revised manuscript received 8 April 2016; published 6 May 2016)

We consider the problem of transport through a multiterminal molecular junction in the presence of a stochastic bias, which can also be used to describe transport through fluctuating molecular energy levels. To describe these effects, we first make a simple extension of our previous work [Phys. Rev. B **91**, 125433 (2015)] to show that the problem of tunneling through noisy energy levels can be mapped onto the problem of a noisy driving bias, which appears in the Kadanoff-Baym equations for this system in an analogous manner to the driving term in the Langevin equation for a classical circuit. This formalism uses the nonequilibrium Green's function method to obtain analytically closed formulas for transport quantities within the wide-band limit approximation for an arbitrary time-dependent bias and it is automatically partition free. We obtain exact closed formulas for both the colored and white noise-averaged current at all times. In the long-time limit, these formulas possess a Landauer-Büttiker–type structure which enables the extraction of an effective transmission coefficient for the transport. Expanding the Fermi function into a series of simple poles, we find an exact formal relation between the parameters which characterize the bias fluctuations and the poles of the Fermi function. This enables us to describe the effect of the temperature and the strength of the fluctuations on the averaged current which we interpret as a quantum analog to the classical fluctuation-dissipation theorem. We use these results to convincingly refute some recent results on the multistability of the current through a fluctuating level, simultaneously verifying that our formalism satisfies some well-known theorems on the asymptotic current. Finally, we present numerical results for the current through a molecular chain which demonstrate a transition from nonlinear to linear I-V characteristics as the strength of fluctuations is increased, as well as a stochastic resonance effect in the conductance of this system.

DOI: 10.1103/PhysRevB.93.205408

I. INTRODUCTION

In classical conductors, the effects of a fluctuating voltage on the current characteristics have been well understood since 1928. In this landmark year for classical electronics, a linear relationship was found to hold between the fluctuation strength of the potential difference and both the electrical resistance of a conductor and its temperature. This relationship was demonstrated first in experimental work carried out by Johnson [1], and then explained in a theoretical model proposed by Nyquist [2]. The so-called Nyquist theorem has found wide applications in classical thermoelectric systems, but has an additional historical significance as one of the first statements of the *fluctuation-dissipation theorem* [3]. The (classical) fluctuation-dissipation theorem states that, in all linear dissipative systems driven by a fluctuating generalized force, the friction (or admittance) of the system is proportional to the magnitude of the fluctuations in the force and to the temperature [4–6]. Another example is provided by the Brownian particle, whose friction coefficient is directly proportional to the correlation function of the random force and to the temperature [5]. The possibility of fluctuation-driven transport of Brownian particles through spatially asymmetric systems has stimulated a great deal of research during the past two decades [7–12], and has been shown to enhance the signal at certain resonant values of the parameters characterizing the noise, in a phenomenon known as *stochastic resonance* [13–17]. These studies involve the solution of a Langevin equation for the particle mobility and include periodically driven systems with various types of added stochasticity [18–23]. The exciting possibility of stochastically enhanced quantum transport has been demonstrated in recent theoretical studies which use a master equation approach to treat exciton transport in photosynthetic systems [24,25]. These studies have shown that a noisy environment can simultaneously destroy quantum coherence whilst enhancing the system transmission. This effect occurs when environmental perturbations open up new channels for excitation transfer, and was verified experimentally in related work on optical cavity networks [26].

Whereas the classical electronic response to a fluctuating bias is well characterized, the analogous physics in nanoscale electronic devices has only recently begun to be explored [27–31]. A typical molecular junction is portrayed schematically in Fig. 1, consisting of a central molecular structure C coupled to two leads L and R. The leads serve as reservoirs for the electrons, which propagate to the C region and scatter on the potential of the molecule. The extension to multiterminal nanojunctions is trivial theoretically and has been realized in several recent experiments [32,33].

In the vast majority of work done on molecular transport to date, the conducting molecule is assumed to possess a static conformation, and the accessible energies on the molecule are contained within a time-independent Hamiltonian [34–37]. Initially, each lead is kept at temperature T and chemical potential μ, before a bias V_α is added to lead α at the switch-on time t_0. The most physically intuitive and popular approach to the calculation of the nanoscale current response to the bias switch-on is provided by the Landauer-Büttiker (LB) formalism [38–41], which expresses the current in lead α of a multilead system in terms of an energy-dependent transmission probability $T_{\gamma\alpha}(\omega)$ between leads γ and α multiplying the

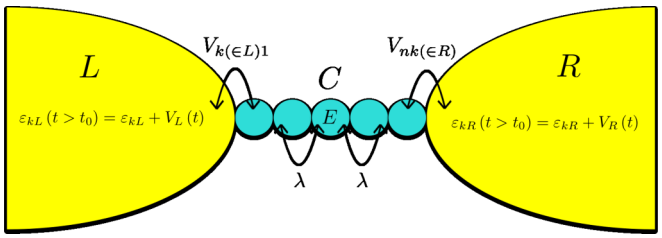


FIG. 1. Schematic of a typical two-lead molecular junction consisting of the left (L) and right (R) leads bridged by a molecular system (C). In this schematic, C is a molecular wire composed of $N_s = 5$ atomic sites with nearest-neighbor hopping.

difference in Fermi functions of the leads:

$$I_\alpha = \frac{1}{\pi}\sum_\gamma \int d\omega\,[f(\omega - V_\alpha - \mu) - f(\omega - V_\gamma - \mu)]T_{\gamma\alpha}(\omega). \quad (1)$$

This expression (1) suggests the interpretation of $T_{\gamma\alpha}$ as the probability for an electron in lead γ to be scattered into lead α. This formula is valid at long times after the switch-on of a constant bias, when the system has relaxed into an ideal steady state [42]. The problem of static transport therefore reduces to calculation of the $T_{\gamma\alpha}$, which can be done, e.g., using scattering state solutions of the time-independent Schrödinger equation [41]. For future reference, any description of a formula as being of the LB type means that it has the same mathematical structure as Eq. (1).

However, the assumption that the molecular energies and external bias are fixed in time will not be true in real systems, where the energies on the molecule are caused to fluctuate rapidly, i.e., for molecules immersed in a solution [30,43,44]. One of the first papers to acknowledge this fact was that of German *et al.*, in which effective transmission probability functions were derived for electron tunneling through a fluctuating single level [27]. In this paper, a negative exponential two-time correlation function was used for the random part of the site energy, so that the interplay between the strength of fluctuations, environment-dot coupling strength, and correlation time could be analyzed. An approach based on transition state theory was later used to study hopping transport through a one-dimensional (1D) molecular chain whose sites fluctuate in time due to electron-electron interactions [45]. One may also consider another source of fluctuations in the junction of Fig. 1: random fluctuations of the bias applied to the leads, which is the quantum analog of the Nyquist problem. This kind of stochasticity has been studied experimentally in carbon nanotube field effect transistors [46,47] and in bistable nanoscale switches [48,49], where an enhancement of the switching due to stochastic resonance was observed. Both kinds of noise, the random fluctuations of the molecular levels and of the applied bias, can effect the current passing through the system, and addressing these is the main objective of our paper.

To tackle the general problem of electron transport through a molecule with stochastic levels (applied bias), it is necessary to go beyond static transport schemes and use methods in which explicit time dependence can be taken into account. One such approach is based on the nonequilibrium Green's function (NEGF) formalism, an extremely general method for the computation of time-dependent ensemble averages [42,50–53]. It involves the solution of the Kadanoff-Baym (KB) equations, a set of integrodifferential equations for various components of the two-time Green's function, with integrals taken over a complex time contour. A numerical propagation scheme based on NEGF has been used to study time-dependent (TD) transport through a single fluctuating level, and analytic results were obtained for this system which confirm the numerics [29]. In this work, a stochastic resonance effect was observed in the current characteristics of a quantum dot system. In addition, a recent study investigated the problem of fluctuating site energies using a numerical time-stepping method based upon the NEGF formalism [30]. They compared numerical results of this TD-NEGF scheme with those obtained from the static LB formula (1), into which a "snapshot" of the system parameters is substituted at each time step. As expected, they found that static snapshot approaches to fast fluctuating systems cannot be accurate because they omit nonadiabatic effects such as ultrafast dephasing due to the presence of transient modes, and changes in the amplification of the current response.

Recently, we presented a TD-NEGF approach which was shown to capture all these time-dependent features, amongst others [54,55]. In this work, we assumed the electrons to be noninteracting and also used the wide-band limit approximation (WBLA), which neglects the frequency dependence of the embedding self-energies. This led us to an exact closed solution to the Kadanoff-Baym equations for a system subjected to an arbitrary time-dependent spatially homogeneous bias in the leads. A closed integral formula was then obtained for the current in lead α, into which the time-dependent bias $V_\alpha(t)$ enters exclusively in the form of phase factors:

$$e^{i\psi_\alpha(t_1,t_2)} \equiv \exp\left(i\int_{t_2}^{t_1} d\tau\, V_\alpha(\tau)\right). \quad (2)$$

In both our previous work [54] and this paper, we set $\hbar = 1$ and work in arbitrary units. The real advance of our formalism on earlier work was to combine explicit time dependence with the partition-free approach developed first by Stefanucci and Almbladh [56], and later extended to a closed formula for the current response to a static bias switch-on which includes short-time transient effects [42,57]. In partition-free approaches, the lead-molecule coupling is present in the Hamiltonian at equilibrium, prior to the switch-on of a bias. In partitioned approaches, the lead-molecule coupling and the bias are added to the Hamiltonian at t_0 simultaneously [58]. This is unlike the situation in real experiments, where the leads equilibrate with the molecule prior to the bias switch-on time t_0 [59], making a partition-free approach a necessity for an accurate description of the transient regime. In Ref. [56], it was proven that the long-time limit of the current does not differ depending on whether the partitioned or partition-free approaches are taken (the theorem of equivalence), and that it is a unique function of the bias if the bias tends to a fixed value in the long-time limit (the memory-loss theorem). A recent numerical work on noninteracting transport through a single fluctuating level [31] has recently made several questionable

claims, e.g., the claim that colored noise fluctuations can be switched on and off but still affect the long-time value of the current, thereby violating the memory-loss theorem. An analytic model which can resolve this apparent contradiction is therefore highly desirable.

To tackle the problems of fluctuations in the molecular levels and the applied bias, we first in Sec. II generalize the formalism developed in [54] to the case in which the system, driven by an arbitrary time-dependent bias on each lead, is also subjected to a time-dependent spatially homogeneous perturbation on the molecule. This leads us to a proof of the physically intuitive equivalence between shifting all the molecular energies by a time-dependent quantity, and shifting all the leads by the same amount. This fact enables us to treat both kinds of stochastic influence on the same formal footing. Modern derivations of the Nyquist theorem use a Langevin equation approach to solve for the electric current, in which the stochastic bias acts as the generalized fluctuating force [3]. In Sec. III, we consider the quantum-statistical analog to the Langevin equation, in which the time-dependent inhomogeneities in the KB equations fluctuate in time. The bias in each lead contains a Gaussian stochastic part with negative exponential correlation function, characterized by the correlation time τ_c and fluctuation strength D. From a general expression for the current averaged with respect to the fluctuating bias, we first consider the quasistatic limit of large τ_c, and find an an exact analytical formula for the current average. This expression is of the LB type in the steady-state limit, so that a closed expression can be found for an effective transmission function, which reduces to the formula in [27] for transmission through a fluctuating dot level. Next, we obtain a general formula for the average current for any τ_c, expressed in powers of $D\tau_c$. This new formula contains the transient which follows the switch-on of the noisy bias. In addition, those terms due to the system preparation can also be identified and are shown to vanish at long times, which demonstrate once again the equivalence of the partitioned and partition-free approaches at long times, even when the driving field is stochastic. The resulting formula for the current also has the particular virtue that it takes an asymptotic (long-time) value which is of the LB form (1), and we can therefore extract an effective transmission function from it. In the $\tau_c \to 0$ limit of white noise fluctuations, this transmission function again reduces to the one published in [27]. We next present a numerical scheme for calculating the current response to a noisy bias, based on the Matsubara expansion of the current formula which removes all frequency integrals. This massively increases the computational efficiency of this method and makes fast calculation of noisy transport through complex nanostructures (for instance, graphene nanoribbons [60]) a real possibility. We show that for arbitrary extended systems, the fluctuations effectively modify the complex poles of the Fermi distribution function, so that the effect of fluctuations is equivalent to a thermal "smearing" of resonances in the transmission function. We interpret this as a *generalized fluctuation-dissipation relation* for quantum transport. We end Sec. III with a demonstration that our current formula satisfies the memory-loss theorem, and we go on to find direct counterproofs to each of the main claims of Ref. [31]. Finally, in Sec. IV we apply this numerical scheme to the problem of tunneling through the five-site molecular wire illustrated in Fig. 1, in both the transient and steady-state regimes. We find that there is a transition from nonlinear to Ohmic behavior in the I-V characteristics of the steady-state current as the fluctuation parameter D is increased. In addition, we observe the existence of a stochastic resonance effect in the conductance spectrum of the molecular wire.

II. GENERALIZED TD-LB FORMALISM

A. Hamiltonian on the contour

The NEGF formalism can be used to calculate ensemble averages at times t following the switch-on event at t_0, which sends the system out of equilibrium. In this section, we specify a Hamiltonian which is very similar to the one in Ref. [54], but here that work will be extended to a slightly more general class of systems. The Hamiltonian for the system is specified everywhere on the so-called Konstantinov-Perel' contour, which consists of an "upper" branch C_-, running from $t_0 + i0$ to $t + i0$, a "lower" branch C_+ running back from $t - i0$ to $t_0 - i0$, and a vertical branch C_M from $t_0 - i0$ to $t_0 - i\beta$ (where $\beta \equiv 1/k_B T$ is the inverse temperature) that corresponds to the equilibrium state of the system. The variable z denotes the contour "time" variable on the Konstantinov-Perel' contour, so that the Hamiltonian operator $\widehat{H}(z)$ appearing in the contour equations of motion describes the system both in equilibrium, and when it has been driven away from equilibrium by the switch-on of the bias. We may write the Hamiltonian as

$$\widehat{H}(z) = \sum_{ij} h_{ij}(z)\hat{d}_i^\dagger \hat{d}_j, \tag{3}$$

where we sum over all orbitals i, j of the leads and the central system. Here, d_i ($d_i^\dagger$) correspond to the annihilation (creation) operators of either the leads or the C region. The $h_{ij}(z)$ are elements of a matrix $\mathbf{h}(z)$, which can be conveniently sectioned into blocks, obtained by projecting it onto the molecule or lead subspaces. $\mathbf{h}_{\alpha C}(z)$ is the block of $\mathbf{h}(z)$ with matrix elements $[\mathbf{h}_{\alpha C}(z)]_{km} = T_{k\alpha,m}(z)$ that describe the coupling between lead α states (labeled $k\alpha$) and molecular states (labeled m). $\mathbf{h}_{CC}(z)$ is the block of $\mathbf{h}(z)$ with matrix elements $[\mathbf{h}_{CC}(z)]_{mn} = T_{mn}(z)$ that describe both the hopping processes and the onsite potential within the molecular region. We furthermore assume that there is no lead-lead coupling, so that $\mathbf{h}_{\alpha\gamma} = \delta_{\alpha\gamma}\mathbf{h}_{\alpha\alpha}$, and we can identify the "bare" lead blocks of $\mathbf{h}(z)$ with matrix elements $[\mathbf{h}_{\alpha\gamma}(z)]_{kk'} = \delta_{\alpha\gamma}\delta_{kk'}\varepsilon_{k\alpha}(z)$. The Hamiltonian matrix thus has the structure

$$\mathbf{h}(z) = \begin{pmatrix} \mathbf{h}_{11}(z) & 0 & \dots & \mathbf{h}_{1C}(z) \\ 0 & \mathbf{h}_{22}(z) & \dots & \mathbf{h}_{2C}(z) \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{h}_{C1}(z) & \mathbf{h}_{C2}(z) & \dots & \mathbf{h}_{CC}(z) \end{pmatrix}. \tag{4}$$

The contour formalism provides an elegant way of understanding the difference between partitioned and partition-free approaches: in the former, the lead-molecule "blocks" $\mathbf{h}_{\alpha C}(z) = 0$ for all $z \in C_M$, whereas in the latter case it

generally holds that for any z, $\mathbf{h}_{\alpha C}(z) \neq 0$. We assume that prior to the switch-on at time t_0 the whole electronic system was in thermodynamic equilibrium characterized by the unique chemical potential μ and inverse temperature β. Then, at t_0 the battery of the external circuit is used to apply an arbitrary time-dependent bias $V_\alpha(t)$ to each lead α.

Our modification to the Hamiltonian studied in [54] is to alter the molecular energy integrals as follows for $t \geqslant t_0$:

$$\begin{aligned}\mathbf{h}_{CC}(t > t_0) &= \mathbf{h}_{CC} + \mathbf{u}_{CC} + V_C(t)\mathbf{I}_{CC} \\ &\equiv \widetilde{\mathbf{h}}_{CC} + V_C(t)\mathbf{I}_{CC}. \end{aligned} \tag{5}$$

Here, $\mathbf{u}_{CC}$ is in general a nondiagonal time-constant matrix, considered, e.g., in Ref. [60], introduced to enable description of a switch-on of a static field in the central region. The last term is diagonal and corresponds to a time-dependent perturbation that factorizes into a time-dependent scalar $V_C(t)$ and the particle number of the CC region. This type of modification of the molecular Hamiltonian was considered in a recent model of a carbon nanotube quantum pump [61], and in Ref. [62], where time-dependent modulation of the lead-molecule coupling was also considered.

Hence, each block of the nanojunction Hamiltonian at every contour time z is specified as follows:

$$[\mathbf{h}_{\alpha\alpha}(z)]_{kk'} = \begin{cases} [\varepsilon_{k\alpha} + V_\alpha(t)]\delta_{kk'}, & z \equiv t \in C_- \oplus C_+ \\ (\varepsilon_{k\alpha} - \mu)\delta_{kk'}, & z \in C_M \end{cases} \tag{6}$$

$$[\mathbf{h}_{C\alpha}(z)]_{mk} = T_{m,k\alpha}, \quad z \in \gamma \tag{7}$$

$$[\mathbf{h}_{CC}(z)]_{mn} = \begin{cases} h_{mn} + u_{mn} + V_C(t)\delta_{mn}, & z \in C_- \oplus C_+ \\ h_{mn} - \mu\delta_{mn}, & z \in C_M. \end{cases} \tag{8}$$

This Hamiltonian describes a nanojunction which has a time-dependent bias switched on in the leads, simultaneously with a spatially homogeneous time-dependent shift of the molecular energy levels.

B. TD-NEGF formalism for the current

We now briefly describe the main features and results of the TD-NEGF formalism that we will use to model systems described by the Hamiltonian of Sec. II A. We first define in the molecular basis the i,jth component of the one-particle Green's function on the Konstantinov-Perel' contour:

$$G_{ij}(z_1,z_2) = -i\frac{\mathrm{Tr}\left\{e^{-\beta\hat{H}^M}\hat{T}_\gamma[\hat{d}_{i,H}(z_1)\hat{d}^\dagger_{j,H}(z_2)]\right\}}{\mathrm{Tr}\left[e^{-\beta\hat{H}^M}\right]}. \tag{9}$$

The elements G_{ij} of the Green's function form a matrix $\mathbf{G}$ defined on the whole space of orbitals of all leads and the central region; correspondingly, one can introduce diagonal, $\mathbf{G}_{CC}$ and $\mathbf{G}_{\alpha\alpha}$, as well as nondiagonal, $\mathbf{G}_{C\alpha}$ and $\mathbf{G}_{\alpha C}$, blocks of this matrix:

$$\mathbf{G}(z_1,z_2) = \begin{pmatrix} \mathbf{G}_{11}(z_1,z_2) & \mathbf{G}_{12}(z_1,z_2) & \dots & \mathbf{G}_{1C}(z_1,z_2) \\ \mathbf{G}_{21}(z_1,z_2) & \mathbf{G}_{22}(z_1,z_2) & \dots & \mathbf{G}_{2C}(z_1,z_2) \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{G}_{C1}(z_1,z_2) & \mathbf{G}_{C2}(z_1,z_2) & \dots & \mathbf{G}_{CC}(z_1,z_2) \end{pmatrix}. \tag{10}$$

Notice that in this matrix there are lead-lead coupling terms $\mathbf{G}_{\alpha\gamma}$, where $\alpha \neq \gamma$, unlike in the Hamiltonian matrix (4). If one introduces the reduced Green's function $\mathbf{g}_{\alpha\alpha}(z_1,z_2)$ satisfying

$$\left[i\frac{d}{dz_1} - \mathbf{h}_{\alpha\alpha}(z_1)\right]\mathbf{g}_{\alpha\alpha}(z_1,z_2) = \mathbf{1}_{\alpha\alpha}\delta(z_1,z_2), \tag{11}$$

then one can show that the full Green's function $\mathbf{G}_{CC}$ for the central region satisfies the equation of motion [42]

$$\begin{aligned}&\left[i\frac{d}{dz_1} - \mathbf{h}_{CC}(z_1)\right]\mathbf{G}_{CC}(z_1,z_2) \\ &\quad = \mathbf{1}_{CC}\delta(z_1,z_2) + \int_\gamma d\bar{z}\,\Sigma_{CC}(z_1,\bar{z})\mathbf{G}_{CC}(\bar{z},z_2), \end{aligned} \tag{12}$$

where $\mathbf{1}_{CC}$ is the unit matrix defined on the orbitals of C, and

$$\Sigma_{CC}(z_1,z_2) = \sum_\alpha \mathbf{h}_{C\alpha}(z_1)\mathbf{g}_{\alpha\alpha}(z_1,z_2)\mathbf{h}_{\alpha C}(z_2) \tag{13}$$

is the matrix of the embedding self-energy, while the nondiagonal matrix blocks of the Green's function are given by integrals on the contour, e.g.,

$$\mathbf{G}_{\alpha C}(z_1,z_2) = \int_\gamma d\bar{z}\,\mathbf{g}_{\alpha\alpha}(z_1,\bar{z})\mathbf{h}_{\alpha C}(\bar{z})\mathbf{G}_{CC}(\bar{z},z_2). \tag{14}$$

The equation of motion (12), along with its complex conjugate, is then projected onto various subspaces defined by combinations of the two contour times z_1,z_2. These are denoted by superscripts, for example, the "greater" and "lesser" Green's functions (GFs) are denoted $\mathbf{G}^{\gtrless}_{CC}(t_1,t_2)$ and can be used to describe the number of holes/electrons in the molecular region of the nanojunction. Their rigorous definition, and the definitions of the retarded, advanced, left, right, and Matsubara Green's functions, can be found in Ref. [54]. Each type of Green's function so defined obeys a particular equation of motion, and these are referred to collectively as the KB equations. Here, we simply note that the retarded KB equation can be found by application of the Langreth rules [63] to Eq. (12):

$$\begin{aligned}&\left(i\frac{d}{dt_1} - \mathbf{h}_{CC}\right)\mathbf{G}^r_{CC}(t_1,t_2) \\ &\quad = \mathbf{1}_{CC}\delta(t_1 - t_2) + \int_{t_0}^{t} d\bar{t}\,\Sigma^r_{CC}(t_1,\bar{t})\mathbf{G}^r_{CC}(\bar{t},t_2). \end{aligned} \tag{15}$$

On the right-hand side of this expression, there is the retarded component of the effective embedding self-energy

$$\begin{aligned}\left[\Sigma^r_{CC}(t_1,t_2)\right]_{mn} = \sum_\alpha e^{-i\psi_\alpha(t_1,t_2)}\int\frac{d\omega}{2\pi}e^{i\omega(t_1-t_2)} \\ \times\left[\Lambda_{\alpha,mn}(\omega) - \frac{i}{2}\Gamma_{\alpha,mn}(\omega)\right], \end{aligned} \tag{16}$$

where the level-width matrix is defined as

$$\Gamma_{\alpha,mn}(\omega) = 2\pi \sum_k T_{m,k\alpha} T_{k\alpha,n} \delta(\omega - \epsilon_{k\alpha}), \tag{17}$$

which forms a Hilbert transform pair with $\Lambda_{\alpha,mn}(\omega)$. The phase factor $\psi_\alpha(t_1,t_2)$ is defined by Eq. (2). In the WBLA, one replaces all elements $\Gamma_{\alpha,mn}(\omega)$ of the level-width matrix Γ_α with a frequency-independent value $\Gamma_{\alpha,mn}$ (e.g., calculated at the equilibrium Fermi energy ε_α^F of lead α [58], although they could also be considered as fitting parameters). Due to the fact that the coupling matrices $\mathbf{h}_{\alpha C}(z)$ and bare lead matrix $\mathbf{h}_{\alpha\alpha}(z)$ are unchanged from Ref. [54], all the components of the self-energies for the system we consider are the same as in that work, so we do not reproduce them here.

In the derivation of the generalized LB formalism given in [54], in which the bias applied to each lead is time dependent, the retarded/advanced Green's functions $\mathbf{G}^{r/a}_{CC}(t_1,t_2)$ are functions of the time difference $t_1 - t_2$ and can be easily represented in Fourier space. However, a time-dependent gate voltage on the molecule of the form in Eq. (5) means that this is no longer true. For example, the retarded component satisfies the equation of motion

$$\left[i\frac{d}{dt_1} - \widetilde{\mathbf{h}}^{\rm eff}_{CC} \right] \mathbf{G}^r_{CC}(t_1,t_2) = \delta(t_1 - t_2) + V_C(t_1)\mathbf{I}_{CC}\mathbf{G}^r_{CC}(t_1,t_2), \tag{18}$$

where $\widetilde{\mathbf{h}}^{\rm eff}_{CC} \equiv \widetilde{\mathbf{h}}_{CC} - \frac{i}{2}\sum_\alpha \Gamma_\alpha$ is an effective Hamiltonian of the central region, with complex eigenvalues that lead to a finite lifetime of unstable eigenmodes there. Equation (18) has the general solution

$$\mathbf{G}^r_{CC}(t_1,t_2) = -i\theta(t_1 - t_2) e^{-i\widetilde{\mathbf{h}}^{\rm eff}_{CC}(t_1-t_2)} e^{-i\varphi_C(t_1,t_2)}, \tag{19}$$

where we make the definition of the phase factor associated with the molecular time dependence:

$$\varphi_C(t_1,t_2) \equiv \int_{t_2}^{t_1} d\tau\, V_C(\tau). \tag{20}$$

Likewise, the advanced component is given by

$$\mathbf{G}^a_{CC}(t_1,t_2) = i\theta(t_2 - t_1) e^{-i(\widetilde{\mathbf{h}}^{\rm eff}_{CC})^\dagger(t_1-t_2)} e^{-i\varphi_C(t_1,t_2)}. \tag{21}$$

These cannot be represented as functions of a single frequency in Fourier space, and we shall henceforth use these expressions in convolution integrals involving both time arguments. In Appendix A, we present analytic expressions for the other components of $\mathbf{G}_{CC}(z_1,z_2)$, and some details of their derivation. Here, we simply remark that a more compact notation can be used to represent the current and the lesser and greater GFs than was used previously. Specifically, if we introduce the matrix

$$\mathbf{S}_\alpha(t,t_0;\omega) \equiv e^{-i\widetilde{\mathbf{h}}^{\rm eff}_{CC}(t-t_0)} e^{-i\varphi_C(t,t_0)} \left[\mathbf{G}^r_{CC}(\omega) - i\int_{t_0}^{t} d\bar{t}\, e^{-i(\omega\mathbf{1} - \widetilde{\mathbf{h}}^{\rm eff}_{CC})(\bar{t}-t_0)} e^{i(\varphi_C - \psi_\alpha)(\bar{t},t_0)} \right], \tag{22}$$

where $\mathbf{G}^r_{CC}(\omega) = (\omega\mathbf{I} - \mathbf{h}^{\rm eff}_{CC})^{-1}$ (i.e., defined without the tilde on the effective Hamiltonian), and φ_C is defined in Eq. (20), then the greater and lesser GFs can be expressed as follows:

$$\mathbf{G}^{\gtrless}_{CC}(t_1,t_2) = \mp i \int \frac{d\omega}{2\pi} f[\mp(\omega - \mu)] \sum_\gamma \mathbf{S}_\gamma(t_1,t_0;\omega)\Gamma_\gamma \mathbf{S}^\dagger_\gamma(t_2,t_0;\omega). \tag{23}$$

From here on we omit the CC subscript as all Green's functions will be those of the central region. The electric current in lead α is defined as the time derivative of the average charge in that lead, $I_\alpha(t) \equiv q\langle \frac{d\hat{N}_\alpha(t)}{dt} \rangle$ (where due to spin degeneracy $\hat{N}_\alpha = 2 \times \sum_k \hat{d}^\dagger_{k\alpha}\hat{d}_{k\alpha}$). Following the method outlined in Ref. [54], it may be expressed in terms of the $\mathbf{S}_\alpha$ (taking electron charge $q = -1$):

$$I_\alpha(t) = \frac{1}{\pi}\int d\omega f(\omega - \mu)\, {\rm Tr}_C \left[2\,{\rm Re}[i\Gamma_\alpha e^{i\omega(t-t_0)} e^{i\psi_\alpha(t,t_0)} \mathbf{S}_\alpha(t,t_0;\omega)] - \Gamma_\alpha \sum_\gamma \mathbf{S}_\gamma(t,t_0;\omega)\Gamma_\gamma \mathbf{S}^\dagger_\gamma(t,t_0;\omega) \right]. \tag{24}$$

This expression enables us to model electron transport in response to the switch-on of an arbitrary time-dependent bias in the leads, as well as a spatially homogeneous time-dependent perturbation in the molecule, within the WBLA. It represents progress on the work published in [54] because it enables us to study the interplay between the driving fields in the lead and molecular regions, but reduces to the published formula when $\varphi_C = 0$ and $\widetilde{\mathbf{h}}_{CC} = \mathbf{h}_{CC}$. We note in this connection that if $V_\alpha(t) = V(t)$ is independent of the lead index α, and $V(t) = V_C(t)$, then $\psi_\alpha = \varphi_C$ and it follows [from the fact that the explicit time dependence enters into (24) only in the form $e^{i(\psi_\alpha - \varphi_C)(t,t_0)}$] that the current is completely equivalent to that obtained in the static bias case. This is a rather intuitive result: it just means that if all energies in the system are simultaneously raised and lowered in the same way, then there is no effect on the transport through the system; the transport is governed by energy *differences* only. We also observe that it is physically equivalent to choose either (i) $V_C(t) = 0$ and $V_\alpha(t) = V(t)$ for all α or (ii) $V_C(t) = -V(t)$ and $V_\alpha(t) = 0$ for all α. This means that an identical perturbation across all the leads is equivalent to the negation of that perturbation in the CC region alone, and one has a freedom of choice in where to place the time dependence. In the following derivations, we shall assume that the bias is applied only to the leads. Hence, in what follows, $\varphi_C(t_1,t_2) \equiv 0$. For simplicity, we shall assume from now on that the matrix $\mathbf{u} = (u_{mn}) = \mathbf{0}$ and hence $\widetilde{\mathbf{h}}^{\rm eff}_{CC} = \mathbf{h}^{\rm eff}_{CC}$.

III. QUANTUM MODEL OF THE STOCHASTIC BIAS

A. Classical model and the quantum analogy

The problem of transport through a classical circuit with a stochastic applied driving bias has been studied using the Langevin equation method. In the simplest case, one solves the equation which encodes Ohm's law for the current [3,18]

$$L\frac{dI}{dt} + RI(t) = V(t). \tag{25}$$

Here, L and R denote the inductance and resistance of the circuit, respectively. In the simplest case, the driving bias $V(t)$ is zero on average, but "flickers" around this average value so that small bursts of current can be observed through the conductor. If the experiment is carried out over a long enough time, the current averaged across realizations of the experiment will be equal to zero. It is then assumed that the bias is a Gaussian zero-mean process, and that the autocorrelation function of $V(t)$ is localized, such that its statistical weight integrated over all times is proportional to some fixed parameter D which quantifies the fluctuations of the bias. From these assumptions, the current can be found, along with the time-dependent variance of the current, and both contain modes which decay on a time scale of $\tau_r = L/R$. One can also derive the following well-known result, a version of the *second fluctuation-dissipation theorem* [4,64]

$$4DL^2 = J_V(\omega = 0) = 4Rk_BT, \tag{26}$$

where $J_V(\omega)$ is the power spectrum of the bias fluctuations defined for positive frequencies. The expression (26) states the direct equivalence of the resistance of the conductor R and fluctuations of the bias, quantified by D, which at first sight appear to have a disconnected physical origin. The reason for this equivalence is that in a macroscopic conductor, both the macroscopic resistance of the circuit and the fluctuations of the bias arise from thermal motion of charge carriers [4].

This observation provides us with indications of the qualitative behavior to look for in the analogous nanojunction. To study such a junction, we specialize the formalism described in Sec. II to the situation in which a bias in each lead is switched on at t_0 before fluctuating about some mean value V_α. The stochastic bias in lead α has the form

$$V_\alpha(t > t_0) = V_\alpha + V^s(t). \tag{27}$$

Here, $V^s_\alpha(t)$ is assumed to be zero-mean, stationary, Gaussian stochastic process. This means that even-ordered statistical moments can be decomposed into products of pair correlation functions, and odd-ordered moments vanish:

$$\overline{V^s(t)} = 0, \tag{28}$$

$$\overline{V^s(t_1)V^s(t_2)} = \overline{V^s(t_1 - t_2)V^s(0)} = C(t_1 - t_2), \tag{29}$$

$$\overline{V^s(t_1)\dots V^s(t_{2n})} = \sum_p C\left(t_{p_1} - t_{p_2}\right)\dots C\left(t_{p_{2n-1}} - t_{p_{2n}}\right), \tag{30}$$

$$\overline{V^s(t_1)\dots V^s(t_{2n+1})} = 0. \tag{31}$$

$\sum_p$ denotes a summation over all permutations of pairs of the time variables, and the bar denotes the average taken with respect to the stochastic bias. From the discussion in Sec. II B, this is equivalent to assuming that the driving term $V_C(t)$ on the right-hand side of the Kadanoff-Baym equations is stochastic, and equal to $-V^s(t)$, with a constant bias V_α switched on in each lead. In analogy with the classical approach in [3], we assume that

$$\int_{-\infty}^{\infty} d\tau\, \overline{V^s(\tau)V^s(0)} = 2D, \tag{32}$$

where D is some parameter characterizing the magnitude of bias fluctuations. As noted in the Introduction, the time-dependent stochastic bias enters into our formula for the current via exponential factors of the form (2), so we make use of the following general theorem for taking the average of these [65]:

$$\begin{aligned}\overline{e^{\pm i\varphi^s(t_2,t_1)}} &\equiv \overline{\exp\left(\pm i\int_{t_1}^{t_2} d\tau\, V^s(\tau)\right)} \\ &= \exp\left[-\frac{1}{2}\int_{t_1}^{t_2} d\tau_1 \int_{t_1}^{t_2} d\tau_2 C(\tau_1 - \tau_2)\right].\end{aligned} \tag{33}$$

Note that $C(\tau_1 - \tau_2)$ is independent of the sign on $V^s(t)$ so that an expression containing an average of the form (33) will be identical to one in which all energies on the molecule are shifted by $\pm V^s(t)$. To proceed further with numerical implementations, one needs to assume a specific functional form for $C(\tau_1 - \tau_2)$. In the simplest case, the white noise correlation function is assumed:

$$C(\tau_1 - \tau_2) = 2D\delta(\tau_1 - \tau_2). \tag{34}$$

Noting that the value of the function (33) must be invariant under the exchange $t_1 \leftrightarrow t_2$, we see that for the white noise stochastic bias it must be given by

$$\overline{e^{\pm i\varphi^s(t_2,t_1)}} = e^{-D|t_1 - t_2|}. \tag{35}$$

One may also choose a correlation function which involves a parameter $\omega_c = 1/\tau_c$, defining a finite correlation time τ_c, over which the bias is statistically correlated:

$$C(\tau_1 - \tau_2) = D\omega_c e^{-\omega_c|\tau_1 - \tau_2|}. \tag{36}$$

This correlator arises, e.g., in approximate microscopic models of molecular energy level fluctuations caused by electron-phonon interactions, in which case ω_c is a measure of the phononic band width [66,67]. It should be noted that this means of incorporating the effects of a phononic environment on the molecule is valid only for T greater than the Debye temperature [68]. Inserting (36) into (33) gives

$$\overline{e^{\pm i\varphi^s(t_2,t_1)}} = \exp\left\{-D\left[|t_1 - t_2| - \frac{1}{\omega_c}(1 - e^{-\omega_c|t_1 - t_2|})\right]\right\}. \tag{37}$$

In the case of the white noise, the correlation time is zero. Notice that the expression (37) tends to the white noise expression (35) in the $\omega_c \to \infty$ limit, and that (37) tends to 1 when $\omega_c \to 0$. Also, we observe that either case satisfies

(32). In practice, values for the fluctuation parameter D may be determined from experiments that measure the two-time correlation function. We could also permit D to have some dependence on ω_c [69]. For example, in the Gauss-Markov model of exciton transport [66,67,70], and in Ref. [27] the correlation function (36) with $D = \sigma^2/\omega_c$ is used, where $\sigma = \sqrt{\overline{[V^s(t)]^2}}$ is the standard deviation of molecular site fluctuations. By the arguments in the previous section, this model is formally equivalent to the one we are considering with a fluctuating bias in the leads. Using the fact that

$$e^{\pm i\varphi^s(t_2,t_1)}e^{\pm i\varphi^s(t_1,t_3)} = e^{\pm i\varphi^s(t_2,t_3)}, \tag{38}$$

we can perform the average over the stochastic bias on the leads in formula (24) and write in expanded form the bias-averaged current:

$$\begin{aligned}\overline{I_\alpha(t)} = \frac{1}{\pi}\int d\omega\, f(\omega-\mu)\mathrm{Tr}_C\Gamma_\alpha\Bigg\{&2\,\mathrm{Re}\Bigg(ie^{i(\omega+V_\alpha-\mathbf{h}^{\mathrm{eff}}_{CC})(t-t_0)}\overline{e^{i\varphi^s(t,t_0)}}\mathbf{G}^r(\omega)+\int_{t_0}^{t}d\tau e^{i(\omega+V_\alpha-\mathbf{h}^{\mathrm{eff}}_{CC})(t-\tau)}\overline{e^{i\varphi^s(t,\tau)}}\Bigg)\\
&-e^{-i\mathbf{h}^{\mathrm{eff}}_{CC}(t-t_0)}\sum_\gamma\Bigg[\mathbf{G}^r(\omega)\Gamma_\gamma\mathbf{G}^a(\omega)+2\,\mathrm{Re}\Bigg(i\mathbf{G}^r(\omega)\Gamma_\gamma\int_{t_0}^{t}d\tau e^{i(\omega+V_\gamma-\mathbf{h}^{\mathrm{eff}\dagger}_{CC})(\tau-t_0)}\overline{e^{i\varphi^s(\tau,t_0)}}\Bigg)\\
&+\int_{t_0}^{t}d\tau\int_{t_0}^{t}d\bar\tau\, e^{-i(\omega+V_\gamma-\mathbf{h}^{\mathrm{eff}}_{CC})(\tau-t_0)}\Gamma_\gamma e^{i(\omega+V_\gamma-\mathbf{h}^{\mathrm{eff}\dagger}_{CC})(\bar\tau-t_0)}\overline{e^{-i\varphi^s(\tau,\bar\tau)}}\Bigg]e^{i\mathbf{h}^{\mathrm{eff}\dagger}_{CC}(t-t_0)}\Bigg\},\end{aligned} \tag{39}$$

where the averages of the exponential bias-containing terms are given by (37). This general formula is the central result of this paper. We drop the CC notation on Green's functions defined in the molecular region basis for notational simplicity. In the last term of Eq. (39), the double integral is in general no longer separable into single integrals over the variables τ, $\bar\tau$ due to the presence of the phase average which binds these variables into a single function of the difference $\tau-\bar\tau$. This leads to slight mathematical complications which will be addressed in Secs. III B and III C. Due to the grouplike property (38), one can similarly derive an expression for the current-current two-time correlation function $\overline{I_\alpha(t)I_\alpha(t')}$, which depends on both times t, t', and not only on their difference.

B. Quasistatic limit

Before proceeding to develop the full theory for a Gaussian color noise with correlation function given by (36), we present results for the quasistatic limit of large τ_c. This corresponds to a stochastic bias that undergoes fluctuations over a very long time scale relative to the intrinsic time scales of the nanojunction. This case was addressed in Ref. [27] for the single-level CC region, so it provides an important check on the validity of our theory. Expanding the exponent in (37) in powers of ω_c and keeping only the first term, we find that the phase factor is effectively replaced by a Gaussian:

$$\overline{e^{\pm i\varphi^s(t_2,t_1)}} \simeq \exp\left[-\tfrac{1}{2}D\omega_c|t_2-t_1|^2\right]. \tag{40}$$

Notice that in the limit of $\omega_c\to 0$, (40) tends to 1, because in this limit $V^s(t)$ is frozen at its mean value of 0 and therefore this case is equivalent to the limiting case of a static bias switch-on process. This expression is then substituted into (39), and all time integrals can be analytically performed. As detailed in Appendix B, this is only possible if we follow Ref. [60] and project the current formula onto the right and left eigenvectors of the matrix $\mathbf{h}^{\mathrm{eff}}_{CC}$:

$$\mathbf{h}^{\mathrm{eff}}_{CC}|\varphi_i^R\rangle = \bar\varepsilon_i|\varphi_i^R\rangle;\quad \langle\varphi_i^L|\mathbf{h}^{\mathrm{eff}}_{CC} = \bar\varepsilon_i\langle\varphi_i^L|. \tag{41}$$

Generally speaking, $|\varphi_j^R\rangle \neq |\varphi_j^L\rangle$ because $\mathbf{h}^{\mathrm{eff}}_{CC}$ is non-Hermitian, and the eigenenergies $\bar\varepsilon_i$ are complex due to the presence of $-i\frac{\Gamma}{2}$ in $\mathbf{h}^{\mathrm{eff}}_{CC}$. The full derivation of the current is given in Appendix B; here, we only note that in the long-time limit it reduces to an expression which is of the LB type:

$$\begin{aligned}\lim_{t_0\to-\infty}\overline{I_\alpha(t)} = \frac{1}{\pi}\sum_\gamma\int d\omega[&f(\omega-V_\alpha-\mu)\\
&-f(\omega-V_\gamma-\mu)]T_{\gamma\alpha}(\omega)\end{aligned} \tag{42}$$

with

$$\begin{aligned}T_{\gamma\alpha}(\omega) = \sqrt{\frac{\pi}{2D\omega_c}}\sum_{j,k}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle i(\bar\varepsilon_j-\bar\varepsilon_k^*)}\\
\times\left\{e^{-\frac{(\omega-\bar\varepsilon_j)^2}{2D\omega_c}}\left[1+\mathrm{erf}\left(i\frac{(\omega-\bar\varepsilon_j)}{\sqrt{2\pi D\omega_c}}\right)\right]+\mathrm{c.c.}_{j\leftrightarrow k}\right\},\end{aligned} \tag{43}$$

where we denote $\mathrm{c.c.}_{j\leftrightarrow k}$ to denote the complex conjugation of the preceding term with indices j and k exchanged. At first sight, this expression bears little resemblance to the formula obtained in [27] for the high-τ_c transmission probability, which is a convolution integral of Gaussian and Lorentzian functions. To illustrate the connection with their work, we specialize to a system consisting of a quantum dot sandwiched between two terminals, such that $\bar\varepsilon_j = \varepsilon_0 - i\frac{\Gamma}{2}$, where ε_0 is the dot energy, Γ a scalar and $\bar\varepsilon_j - \bar\varepsilon_k^* = -i\Gamma$. In this case, the transmission probability for electron to pass from lead γ to lead α becomes

$$\begin{aligned}T_{\gamma\alpha}(\omega) &= \sqrt{\frac{2\pi}{D\omega_c}}\frac{\Gamma_\alpha\Gamma_\gamma}{\Gamma}\mathbb{V}\left(\frac{\Gamma}{2\sqrt{2D\omega_c}},\frac{-(\omega-\varepsilon_0)}{\sqrt{2D\omega_c}}\right)\\
&= \frac{1}{\sqrt{2\pi D\omega_c}}\int_{-\infty}^{\infty}d\varepsilon'\frac{\Gamma_\alpha\Gamma_\gamma}{(\omega-\varepsilon_0-\varepsilon')^2+\Gamma^2/4}\\
&\quad\times\exp\left(-\frac{\varepsilon'^2}{2D\omega_c}\right),\end{aligned} \tag{44}$$

where

$$\mathbb{V}(a,b) \equiv \frac{a}{\pi}\int_{-\infty}^{\infty} dz\, \frac{e^{-z^2}}{(z-b)^2+a^2} = \mathrm{Re}\left[e^{(a+ib)^2}[1-\mathrm{erf}(a+ib)]\right] \quad (45)$$

is the *Voigt function* [71,72].

If one makes the replacement $D \to \sigma^2/\omega_c$, one sees that the expression (44) is identical to the formula (12) in Ref. [27], which was obtained by completely different means. We emphasize that our approach is much more general than that of German *et al.* because it generalizes their formula for the transmission function to multiple leads and a multilevel Hamiltonian. Most significantly for this work, it enables us to study the effect of a strongly correlated energy fluctuation on the transport in all time regimes, for both the partitioned and partition-free switch-on processes.

C. Expansion for arbitrary τ_c

1. *Effective transmission and the white noise limit*

A general theory of fluctuating-bias driven transport must include calculation of the current and transmission of a system for all values of the correlation time τ_c, including as a special case the white noise limit described by (34) when $\tau_c \to 0$. To this end, we expand the color noise phase average (37) in powers of $D\tau_c$:

$$\overline{e^{\pm i\varphi^s(t_2,t_1)}} = \sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n \sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}e^{-(D+m\omega_c)|t_2-t_1|}. \quad (46)$$

When we insert (46) into (39), we once again project onto the left/right eigenbasis and evaluate all time integrals explicitly. The details of the resulting formula are given in Appendix C. Here, we focus on the long-time limit when the resulting bias-averaged current converges to a finite value given by a LB-type expression containing an effective transmission probability depending upon both D and ω_c:

$$\lim_{t_0\to-\infty}\overline{I_\alpha(t)} \equiv I_\alpha^{\mathrm{LB}}(D,\omega_c) = \frac{1}{\pi}\sum_\gamma \int d\omega[f(\omega-V_\alpha-\mu) - f(\omega-V_\gamma-\mu)]T_{\gamma\alpha}(\omega,D,\omega_c). \quad (47)$$

We note that those modes of the current which die out, are, as in Ref. [54], exactly those which result from the preparation of the system, and therefore the asymptotic bias-averaged current satisfies the theorem of equivalence; in this limit it has the same value whether one takes the partitioned or the partition-free approach [56]. The effective transmission can be shown to equal a sum of Lorentzians centered on $(\bar{\varepsilon}_j+\bar{\varepsilon}_k^*)/2$ with a level width that increases with D:

$$T_{\gamma\alpha}(\omega,D,\omega_c) = \sum_{j,k}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)}\sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n\sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}\frac{i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)+2(D+m\omega_c)}{\left(\omega-\frac{\bar{\varepsilon}_j+\bar{\varepsilon}_k^*}{2}\right)^2+\frac{1}{4}[i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)+2(D+m\omega_c)]^2}. \quad (48)$$

If the additional assumption is made that all the level width matrices are proportional, i.e., $\Gamma_\gamma = x_\gamma\Gamma$, then the summation indices decouple and (48) is reexpressible as

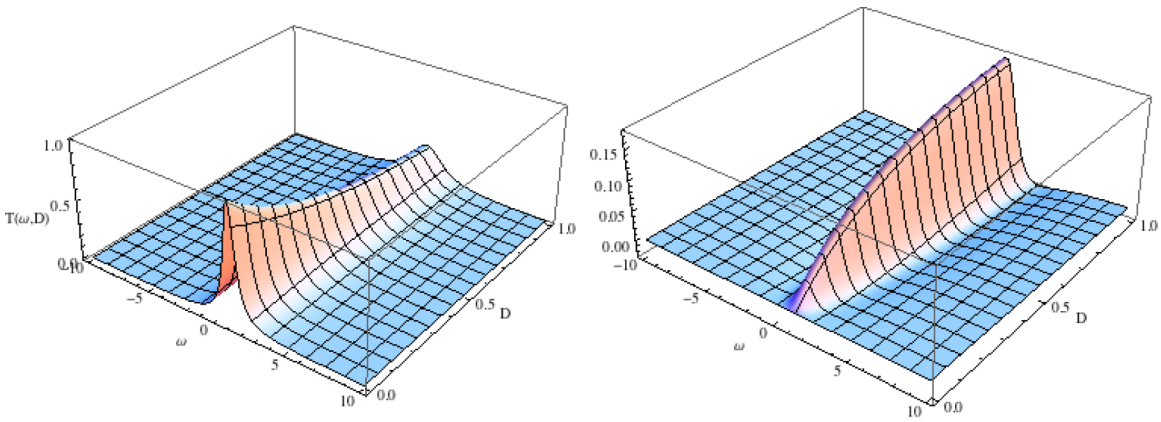
$$T_{\gamma\alpha}(\omega,D,\omega_c) = x_\gamma\sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n\sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}\mathrm{Tr}_C\{\Gamma_\alpha\mathbf{G}^r[\omega+i(D+m\omega_c)][\Gamma+2(D+m\omega_c)]\mathbf{G}^a[\omega-i(D+m\omega_c)]\}. \quad (49)$$

From this result, we can establish a second connection with published work, by taking the white noise limit ($\omega_c \to \infty$) of $T_{\gamma\alpha}(\omega,D,\omega_c)$ and once again considering the simple case of the single-level system studied in Sec. III B. In this limit, all terms in the expansion (49) of the transmission probability vanish with the exception of the $n=0$ mode:

$$\lim_{\omega_c\to\infty}T_{\gamma\alpha}(\omega,D,\omega_c) = \frac{\Gamma_\alpha\Gamma_\gamma}{\Gamma}\frac{\Gamma+2D}{(\omega-\varepsilon_0)^2+(\Gamma/2+D)^2}. \quad (50)$$

This agrees exactly with the formula (15) in Ref. [27]. Clearly, the effect of large fluctuations of the bias about its mean value is to flatten the transmission function and therefore eliminate the resonance at frequencies close to ε_0. The resonance is sharpest at $D=0$, in which case the transmission (50) assumes the well-known Breit-Wigner form [27,42], and the resulting current formula is given exactly by the steady-state LB formula. We remark in passing that the analytic results of Ref. [29] lead to the same effective transmission as Eq. (50) under the appropriate limits.

In Fig. 2(a), we plot the transmission function (50) for a two-lead system with symmetric coupling $\Gamma_L = 0.5 = \Gamma_R$, and dot energy $\varepsilon_0 = 1$. The transmission function is a probability distribution in frequency space, so that by virtue of the Heisenberg energy-time uncertainty principle, we interpret a narrow distribution as corresponding to eigenmodes of the dot with a long lifetime. In all previous treatments of steady-state quantum transport, it has effectively been assumed that $D=0$ so that this lifetime is given by approximately $\tau_{el} \sim 2/\Gamma$. However, here the bias is not assumed perfectly static, but



(a) (b)

FIG. 2. (a) Variation of the frequency-dependent transmission function as the fluctuation parameter D is increased from 0 to 1. (b) Setting $\omega_c = 1$, we plot the difference $T(\omega, D, \omega_c) - T(\omega, D, \omega_c \to \infty)$. Both plots assume coupling parameters $\Gamma_L = 0.5 = \Gamma_R$, and dot energy $\varepsilon_0 = 1$.

is instead allowed to fluctuate about its fixed value, and the lifetime of molecular modes is decreased to $\tau_{el} \sim \frac{1}{\Gamma/2+D}$. This is clearly illustrated by Fig. 2(a), where this decrease of temporal uncertainty is mirrored by a complete flattening out of the transmission function at all frequencies. The qualitative effects of this on the I-V characteristics of a system with white noise fluctuations will be discussed in Sec. IV.

2. *Fluctuation dissipation*

It is a well-known result that, in the steady state following the switch-on of a static bias, the transmission function can be expressed in terms of Green's functions of the CC region [41]:

$$T_{\gamma\alpha}(\omega) \equiv \mathrm{Tr}_C[\Gamma_\alpha \mathbf{G}^r(\omega)\Gamma_\gamma \mathbf{G}^a(\omega)]. \tag{51}$$

On inspection, one can see that for a single-level dot in the $D \to 0$ limit, Eq. (50) reduces exactly to the formula (51) for the transmission function. Therefore, for the case of the quantum dot, the effect of adding a stochastic part to the bias is identical to the effect of adding another lead to the junction with self-energy $-iD\mathbf{I}$, although the two sources of dissipation on the dot are physically distinct. More generally, if one considers the structure of the summand in (49), it is strikingly similar to that of (51). The expression (49) is identical to a weighted sum of transmission functions of the form found in (51) for a molecule whose coupling to each lead $\gamma \neq \alpha$ is enhanced:

$$\Gamma_\gamma \to \Gamma_\gamma + x_\gamma 2(D + m\omega_c)\mathbf{I}. \tag{52}$$

The relation (52) relates the self-energy, which describes the broadening and dephasing of molecular eigenmodes, to the fluctuation of the bias placed across the molecular junction. This is analogous to the Nyquist theorem, which relates fluctuations in the bias to the dissipative quantity R. However, in contrast to the classical circuit, in the quantum case the fluctuations make a modification to the "frictional" term Γ which is *additive*. Formally, the effects are similar to the self-energies used in phenomenological theories of the electron-phonon coupling strength, in which the influence of the e-ph coupling is equivalent to that of a fictitious probe coupled to the system [73,74].

The relation (52) applies only to systems satisfying the condition that $\Gamma_\gamma = x_\gamma \Gamma$, which should hold for very small or dotlike systems, but in other circumstances it is not exact and should only be used to guide physical intuition. It would be desirable to find a general principle that relates the smearing out of quantum features in the transport to the fluctuations in the bias (or, equivalently, of energy levels in the molecule), valid for arbitrary Γ_γ. This can be done if we expand the Fermi function into a sum of N_p simple poles defined in the complex energy plane [75–78]

$$f(x) \equiv \frac{1}{e^{\beta x}+1} = \frac{1}{2} - \lim_{N\to\infty} \sum_{l=1}^{N_p} \eta_l \left[\frac{1}{\beta x + i\zeta_l} + \frac{1}{\beta x - i\zeta_l} \right]. \tag{53}$$

This is equivalent to the well-known Matsubara expansion if we choose $\eta_l = 1$ and $\zeta_l = \pi(2l-1)$. The full formula for the time-dependent current in terms of special functions obtained from a Matsubara expansion is given in Appendix C. However, for numerical implementations, the Padé expansion converges much more rapidly for increasing N_p, and has been used to speed up several time-dependent transport schemes [29,79,80]. In contrast to the Matsubara expansion, the ζ_l are spaced unevenly along the imaginary axis, and the residues η_l are all real and positive valued, obtained from a numerical diagonalization procedure. In either representation, the Fermi function has poles distributed symmetrically along the imaginary axis in the upper and lower half-planes. If the temperature of the system is increased, then each pole ζ_l/β is shifted further away from the real axis; therefore, a uniform shift of all the poles tends to flatten out the Fermi function around $x = 0$, and to "smear" out quantum effects in this region. Inserting Eq. (53) into (47) and performing the resulting contour integrals, we obtain the following formula

for the current in terms of the poles:

$$I_\alpha^{\mathrm{LB}}(D,\omega_c) = \frac{i}{\beta}\sum_\gamma (V_\alpha - V_\gamma)\sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n \sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}\sum_{j,k}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)}$$
$$\times \lim_{N\to\infty}\sum_{l=1}^{N}\eta_l\left[\frac{1}{\left[\bar{\varepsilon}_j - V_\alpha - \mu - i\left(D + m\omega_c + \frac{\zeta_l}{\beta}\right)\right]\left[\bar{\varepsilon}_j - V_\gamma - \mu - i\left(D + m\omega_c + \frac{\zeta_l}{\beta}\right)\right]} + \text{c.c.}_{j\leftrightarrow k}\right]. \quad (54)$$

In the white noise limit, (54) is exactly equal to the regular LB formula, in which all poles of the Fermi function undergo the shift

$$\frac{\zeta_l}{\beta} \to \frac{\zeta_l}{\beta} + D \quad (55)$$

so that the formal effect of the fluctuating white noise bias is therefore to shift all of the poles of the Fermi function lying on the imaginary frequency axis by a constant value D. We expect that this will generate similar physics to an increase in temperature, as the latter change also has the effect of increasing the magnitude of the positive and negative imaginary poles $\pm\frac{\zeta_l}{\beta}$. For the general case of the colored noise, we can assert the following result: *The asymptotic value of the average current through a molecule subject to bias fluctuations with magnitude D and correlation time τ_c is a weighted sum of LB-type formulas evaluated with Fermi functions whose poles are shifted as*

$$\frac{\zeta_l}{\beta} \to \frac{\zeta_l}{\beta} + D + m/\tau_c, \quad (56)$$

where m is an integer.

Although this statement is valid for fluctuations described by the correlation function (36) and hence as such is not completely general, it can obviously be generalized to a correlation function fitted to a sum of negative exponentials and can therefore be used to describe a vast number of Gaussian stochastic processes. We therefore expect that the effect of a nonzero stochastic bias should affect its resistance in a similar (but not identical) way to a temperature increase: at large temperatures, Eq. (54) implies a linear dependence of the resistance on temperature, as in the Nyquist theorem. An exact formula for the multilevel resistance is further illustrated by considering the resistance of the single-level model in Sec. IV. We note in passing that in Ref. [54] we identified those terms in the current which arise from either the initial condition for the lesser Green's function or from vertical contour convolutions. These terms contain information on the way the system was prepared, as they arise from the Matsubara Hamiltonian. One can see during the derivation of Eq. (C5) that those terms which are *not*preparation dependent conform to the relation in Eq. (56). So, we conclude the following: *The relation (56) is also true for all the time-dependent modes of the lesser Green's function and current which arise from real-time convolutions taken on the horizontal part of the Konstantinov-Perel' contour.*

Finally, we can conclude from the LB-type structure of Eq. (54) that, if there is no net bias across the junction, i.e., $V_\alpha = V_\gamma$ for all γ, then no current can flow, regardless of the molecular structure. A *ratchet* is a structure described by a spatially periodic potential $V(x)$ which lacks reflection symmetry, and is of interest for the understanding of transport processes in biological systems, which can efficiently transport molecules across a system with no applied potential or thermal gradient [17,81–83]. Substantial work has been done on directed noise-induced transport resulting from broken symmetries [9,11,20,69]. In particular, it was shown that in ratchet structures a net current can be established from fluctuating forces, given that the fluctuations are non-Gaussian and that all odd statistical moments of the fluctuations are vanishing [20,69]. Furthermore, Łuczka *et al.* demonstrated that if the structure is reflection symmetric, then there is no current unless the fluctuations are *asymmetric*, i.e., with odd-ordered moments that are nonzero [9,11]. Consistently with Eq. (54), this work implies that the quantum ratchet effect cannot be observed in any system if the net bias is zero and the fluctuations are Gaussian. However, in our previous work [54] it was usually assumed that the fluctuations were spatially homogeneous. By contrast, one can show with a straightforward extension [via the replacement $V^s(t) \to V_\alpha^s(t)$] of our formalism that one could generate a net current with zero net bias if the fluctuations in each lead are of a different magnitude, even if they are Gaussian. In this case the fluctuation parameter D acquires a lead index α and the formula for $I_\alpha^{\mathrm{LB}}(D,\omega_c)$ would no longer be of the LB type. The resulting current is a kind of stochastic "pump" as it results from a stochastic dynamical asymmetry in the fluctuating lead Fermi levels, even though there is zero net bias [84]. As we are not focusing on asymmetry effects here, we defer proper investigation of this stochastic pump to a future work.

3. *Multistability and asymptotics*

In Ref. [56], two key theorems of noninteracting quantum transport were established. The first, known as the theorem of equivalence, states that the *long-time limit* of the current response to an arbitrary time-dependent bias is the same for both the partitioned and the partition-free approaches. Our TD-NEGF formula was shown [54] to satisfy this theorem, and so any asymptotic formulas for the current derived in this paper are valid in either framework. The second, called the memory-loss theorem, states that if the bias $V_\alpha(t)$ tends to a static value V_α as $t - t_0 \to \infty$, the current also possesses a unique asymptotic value which is a function of V_α [56]. In Ref. [54], we proved that our formula satisfies this theorem as well and that the value of the asymptotic current is given by an expression of the LB form. A recent paper on transport through a fluctuating level [31] has brought these theorems into question by suggesting that tunneling through a fluctuating energy level can generate multistability in the long-time current in a manner that violates the memory-loss theorem.

Specifically, Ref. [31] considered tunneling through a single fluctuating level of energy ε_0, which is symmetrically coupled to left and right leads, so that the level width matrices become scalars obeying $\Gamma_L = \frac{\Gamma}{2} = \Gamma_R$. They calculated the symmetrized current, which in our formalism can be written as follows:

$$\overline{I_{LR}(t)} \equiv \frac{\overline{I_L(t) - I_R(t)}}{2} = \frac{1}{2\pi}\int d\omega f(\omega-\mu)\mathrm{Re}[i\Gamma e^{i\omega(t-t_0)} \times (\overline{e^{i\psi_L(t,t_0)}S_L(t,t_0;\omega)} - \overline{e^{i\psi_R(t,t_0)}S_R(t,t_0;\omega)})], \quad (57)$$

where S_L, S_R are scalar functions defined as in Eq. (22) and the effective Hamiltonian $\mathbf{h}^{\mathrm{eff}}_{CC} \to h^{\mathrm{eff}} = \varepsilon_0 - i\Gamma/2$. Numerical simulations on this model are reported in [31] which appear to provide support for the following propositions: (i) If the noise on the level is white, then there is no effect on the asymptotic current, even if the noise is present at all times, including in the asymptotic limit. (ii) If the noise on the level is colored and switched on during the transient regime $t \in [t_0, 2/\Gamma]$ following the switch-on, then the asymptotic current is suppressed with respect to its LB value, even if the noise is switched off subsequent to the transient regime. (iii) Any kind of noise switched on only after the transient regime has elapsed (i.e., for $t > 2/\Gamma$) can have no effect on the asymptotic current. In this work, a partitioned approach is used within the WBLA, and in addition to the lead-dot coupling, the dot energy acquires a stochastic time dependence $V(t)$ at time t_0. The method used to establish (i)–(iii) was based on a numerical time-stepping scheme, which calculates long-time currents for different trajectories of $V(t)$ before averaging across the resulting ensemble for the ensemble average of the current.

Clearly, claim (ii) of the above violates the memory-loss theorem because it implies that one can have a static bias in the long-time limit without the corresponding relaxation to a unique value of the current. In addition, (i) implies that one can have a level which is constantly undergoing fluctuations due to interactions with its environment, but if they are completely uncorrelated in time then there is no effect on the transport. (iii) also implies this, but in addition implies that correlated fluctuations also have no effect if they are switched on after the crucial initial period. A complete theory of transport through a fluctuating level must be able to address these rather fundamental claims.

The formula (50) is proof that white noise fluctuations on a dot energy level can affect the asymptotic value of the current passing through it, so long as $\lim_{\tau_c \to 0} D \neq 0$. This contradicts claim (i) of Ref. [31], where it was asserted that the electrons do not "see" the fluctuations in the energy level and so therefore the transport is unaffected. However, there are good physical reasons to suppose the contrary: we have already discussed numerical work in the Introduction where fluctuations lead to changes in the steady-state current [29,30]. Physically, one can see that during the transport process, a dot energy with white noise can jump frequently to values far from the mean energy ε_0. This means that, in the time it takes for an electron to hop across the junction, the energy gradient across the junction can switch sign and the electron has an equal probability to hop in any direction. There is no longer a resonance at ε_0 because electrons with this energy are no longer "privileged" in the transport process with respect to electrons of other energies. In Fig. 2(b), we illustrate the effect of a finite correlation frequency of $\omega_c = 1$ on the transport through the single-level system, by plotting the difference in the transmission (48) and the white noise transmission function (50). We find that as D is increased, this difference grows larger, before flattening out, so that the effect of color noise on the transmission is to slow down its decay with increasing fluctuation strength. Physically, this means that the energies on the dot are not completely random, so there are still some privileged energy values at which the electron will be transported.

Claim (ii) is straightforward to check. Choosing the time t_u as the upper bound of the transient regime, we can simply set $V^s_\alpha(t) = 0$ for any $t > t_u$ [so that $V_\alpha(t) = V_\alpha$ is constant at these times] and evaluate the long-time limit of the main ingredient of the current (24):

$$\lim_{t\to\infty} \overline{e^{i\omega(t-t_0)}e^{i\psi_\alpha(t,t_0)}\mathbf{S}_\alpha(t,t_0;\omega)} = \mathbf{G}^r(\omega + V_\alpha). \quad (58)$$

Indeed, the first term in $e^{i\omega(t-t_0)}e^{i\psi_\alpha}\mathbf{S}_\alpha$ contains the time-decaying exponent $e^{i(\omega\mathbf{1}-\mathbf{h}^{\mathrm{eff}}_{CC})(t-t_0)} \sim e^{-\frac{1}{2}\Gamma(t-t_0)}$, which vanishes in the $t \to \infty$ limit. In the second term

$$-i\int_{t_0}^{t} d\tau e^{i(\omega\mathbf{1}-\mathbf{h}^{\mathrm{eff}}_{CC})(t-\tau)}e^{-i\varphi_\alpha(t,\tau)},$$

we split the integral by the time t_u. The integral over the interval $\bar{t} \in [t_0, t_u]$ vanishes because $e^{-i\mathbf{h}^{\mathrm{eff}}(t-\tau)}$ goes to zero for all τ in this integrand. The second integral taken over the interval $\bar{t} \in [t_u, t]$ can be easily calculated yielding

$$-\mathbf{G}^r(\omega + V_\alpha)[e^{i[(\omega+V_\alpha)\mathbf{1}-\mathbf{h}^{\mathrm{eff}}_{CC}](t-t_0)} - 1].$$

As the exponential term tends to zero at long times, we immediately obtain (58). Replacing $e^{i\omega(t-t_0)}e^{i\psi_\alpha}\mathbf{S}_\alpha$ with $\mathbf{G}^r(\omega + V_\alpha)$ in the formula (24) for the current, we recover the LB formula. Hence, at long times the unique value of the current corresponding to the stationary result is established even if the color noise is only present during the transient. Although this is sufficient to contradict claim (ii) on its own, it is actually a much weaker condition than the memory-loss theorem, which implies that the bias could fluctuate in any way at any finite time, so long as it takes a static value asymptotically, and the value of the current will be a unique function of that value. This theorem can be proven for any system within the WBLA by recognizing that the time t_u can be taken infinitesimally close to t, resulting in the LB value for the asymptotic current even in this case. Thus, we have explicitly verified the memory-loss theorem for any TD bias within the WBLA and ultimately demonstrated that claim (ii) of Ref. [31] is false. As this theorem is true for any realization of the ensemble defined by the noisy bias $V^s_\alpha(t)$, it is also true for the ensemble average, which explains the limit (58).

The equation for the current contains the transient following the switch-on of the noisy bias, and we can therefore use it to verify the validity of claim (iii). We can easily check this by setting $V^s_\alpha(t) = 0$ for $t \in [t_0, t_u]$ and choosing $V^s_\alpha(t)$ as a generic color noise characterized by the parameters D, ω_c. The following limit can then be calculated using the same methods as in Sec. III C, and considering the convergence of

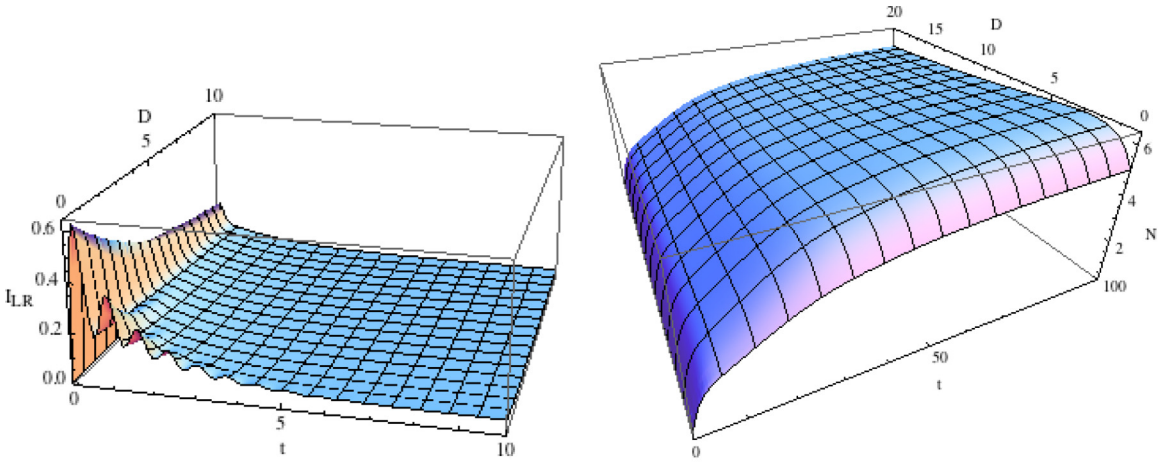


FIG. 3. (a) The time-dependent symmetrized current $\overline{I_{LR}(t)}$ computed as a function of D using parameters $k_BT = 0.1$, $V_L = 10$, $V_R = 0$, $\Gamma_{11} = 0.5$, $\Gamma_{55} = 0.5$, $E = 1$, $\lambda = 0.1$. (b) The time-dependent bias-averaged particle number $\overline{N_C(t)}$ in the molecular wire.

the integrand in the regions $\tau \in [t_0, t_u]$ and $\tau \in [t_u, t]$:

$$\lim_{t\to\infty} e^{i\omega(t-t_0)}\overline{e^{i\psi_\alpha(t,t_0)}S_\alpha(t,t_0;\omega)} = \sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n \sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}G^r[\omega + V_\alpha + i(D + m\omega_c)]. \tag{59}$$

This result is clearly not equal to the final value of $G^r(\omega + V_\alpha)$, which would result from a static bias switch-on process. We note that our conclusion is strongly supported by the numerical work published in Ref. [29]. Therefore, claim (iii) of Ref. [31] is also contradicted because it implies that a constantly fluctuating bias switched on outside the transient period should result in the LB current.

IV. NUMERICS

To get an idea of how the voltage dependence of the current varies with the bias fluctuations, we consider the current through a molecular wire consisting of $N_s = 5$ atoms, coupled to two leads L and R, as illustrated in Fig. 1. This system was previously studied using the method developed in Ref. [55] for a sinusoidal driving bias. We describe this system using a tight-binding model for the wire with nearest-neighbor hopping, as described in [85,86]. Specifically, we assume that there is one state per site (atom) in the chain, and that the interaction of the chain orbitals with those in the leads is only via the end sites. Within the WBLA, the self-energy components are given by Eq. (17), so that in our model only the Γ_{11} and Γ_{55} elements of the self-energy matrix are nonzero. Effectively, we are describing a chain of quantum dots coupled to each other by a nearest-neighbor hopping, leading to a tridiagonal molecular Hamiltonian matrix $\mathbf{h}_{CC}$ with elements $[\mathbf{h}_{CC}]_{k,k} \equiv E$ and $[\mathbf{h}_{CC}]_{k,k+1} = [\mathbf{h}_{CC}]_{k+1,k} \equiv \lambda$ [87,88]. Additionally, we choose the chemical potential $\mu = 0$ and the matrix elements $E = 1$, $\lambda = 0.1$, $\Gamma_{11} = 0.5 = \Gamma_{55}$ which define the energy and time scales in arbitrary units. The mean values of the fluctuating bias are written $\overline{V_L(t)} \equiv V_L$ and $\overline{V_R(t)} \equiv V_R$.

We first consider the effects of white noise on the I-t characteristics of the system, using the formula (C5) with $\tau_c = 0$, $E = 1$, $V_L = 10$, and $V_R = 0$, and using the Padé expansion with $N_p = 20$ to evaluate all special functions. In Fig. 3(a), we plot as a function of both the time t and fluctuation parameter D the long-time average of the symmetrized current, defined for an arbitrary coupling to the leads as

$$\overline{I_{LR}(t)} \equiv \frac{\overline{I_L(t)} - \overline{I_R(t)}}{2}. \tag{60}$$

Whereas for low D there is an oscillatory "ringing" transient signal following the switch-on of the bias, for strong fluctuations these oscillations are washed out. The time-dependent effects of the fluctuation on the decay of modes can be clearly seen in the general formula (C5). The time scale of the decaying modes is influenced by the imaginary part of the complex eigenvalues $\bar{\varepsilon}_j = h_j - i\gamma_j$, from which the decay time can be given roughly as $\tau \equiv \mathrm{Max}\{1/\gamma_j\}$ [55]. In addition to terms for which this is the only source of decay, we note the existence of modes with prefactors of the form $e^{-n\pi k_BT}$ for integer n, so that an increase in temperature has the dynamical effect of pushing the system more rapidly towards its stationary state. Fluctuations on the bias or energy levels increase the rate of decay in these modes of the current, which acquire a prefactor of $e^{-(D+m\omega_c)(t-t_0)}$ for the mth term of the summation. The fluctuations therefore speed up the loss of stable molecular eigenmodes into the leads in a similar (but not exactly equivalent) way to the temperature and the level width Γ, consistently with the discussion of Eqs. (52) and (56) given above. In Fig. 3(b), we show the time dependence of the bias average $\overline{N_C(t)}$ of the particle number $N_C(t) \equiv -2i\,\mathrm{Tr}_C[\mathbf{G}^<_{CC}(t,t)]$, which can be evaluated via the same methods used for the current. The central region undergoes a fast filling process before asymptoting long after the most dramatic oscillations in the current have died down, at $t \sim 100$. This is due to the sparsity of the level width matrix,

as discussed in Ref. [55]. One can show that in the long-time limit the particle number is given by the expression

$$\lim_{t\to\infty}\overline{N_C(t)} = \frac{1}{\pi}\mathrm{Re}\sum_{j,k,\gamma}\frac{\langle\varphi_k^R|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle(\bar{\varepsilon}_k^* - \bar{\varepsilon}_j)}\sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n \times\sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}\left[i\pi + 2\Psi\left(\frac{1}{2} - \frac{\beta}{2i\pi}[\bar{\varepsilon}_j - \mu - V_\alpha - i(D+m\omega_c)]\right)\right]. \tag{61}$$

Here, $\Psi(z) \equiv d\ln\Gamma(z)/dz$ denotes the digamma function, discussed in Appendix C. The plot shows that the steady-state value of $\overline{N_C}$ approaches the half-filled value of 5 as D is increased, a trend that was also seen in Ref. [29]. We can, however, make a more general statement about Eq. (61) in the limit of large D, as the digamma function vanishes and the resulting expression is simplified using the idempotency relation (B1) and the fact that $\langle\varphi_j^L|\Gamma|\varphi_k^R\rangle = -i(\bar{\varepsilon}_k^* - \bar{\varepsilon}_j)\langle\varphi_j^L|\varphi_k^R\rangle$ to give

$$\lim_{D,t\to\infty}\overline{N_C(t)} = \lim_{D\to\infty}\sum_{k=1}^{N_s} e^{D(1-1)/\omega_c} = N_s, \tag{62}$$

i.e., it equals half the number of available states (in a spin degenerate system) for any value of ω_c.

Now, we move to the steady-state regime and focus on the effects of white noise on the I-V characteristics of the system, using the formula (C6). Fixing $V_R = 0$, we vary V_L so that the molecular chain energy levels are always located in the bias window where the transport occurs. In Fig. 4(a), we plot as a function of both the bias $V = V_L - V_R$ and fluctuation parameter D the long-time average of $\overline{I_{LR}(t)}$. In order to focus solely on the effects of the fluctuations, we set $k_BT = 0.1$. Whereas the characteristic nonlinear steplike structure is observed at low values of D [89–94], there appears to be a smooth transition to a linear I-V relation as the magnitude of the bias fluctuations is increased.

In order to rationalize this behavior, we consider the zero-temperature limit of (47) for arbitrary noise. The problem of transport with site fluctuations at low temperature is of specific interest in the Anderson insulator problem considered in Ref. [45]. It also provides us with guidance on the qualitative features one may expect to see in the current as a function of the bias and the fluctuation parameters D and ω_c. The formula (47) in this limit assumes the form

$$\lim_{T\to 0} I_\alpha^{\mathrm{LB}}(D,\omega_c) = \frac{2}{\pi}\sum_{j,k,\gamma}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)}\sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n\sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!} \times\left[\arctan\left(\frac{V_\alpha + \mu - (\bar{\varepsilon}_j + \bar{\varepsilon}_k^*)/2}{D + m\omega_c + i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)/2}\right) - \arctan\left(\frac{V_\gamma + \mu - (\bar{\varepsilon}_j + \bar{\varepsilon}_k^*)/2}{D + m\omega_c + i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)/2}\right)\right]. \tag{63}$$

As D is increased, the region in which the arctan is approximately linear also increases, and the current's dependence on the bias becomes exactly linear, as can be seen from the $D \gg V_{\alpha/\gamma}$ limit of (63):

$$\lim_{T\to 0, D\gg V_{\alpha/\gamma}} I_\alpha^{\mathrm{LB}}(D,\omega_c) \simeq \frac{4}{\pi}\sum_{j,k,\gamma}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \times\left[\sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n\sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}\frac{1}{2(D+m\omega_c) + i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)}\right](V_\alpha - V_\gamma). \tag{64}$$

The obtained expression shows that the fluctuations drive a transition from nonlinearity in the I-V characteristic current to an Ohmic regime. It also demonstrates that, when the noise is white, I_α^{LB} tends to 0 in the $D\to\infty$ limit, i.e., there is zero net current across the nanojunction. This explains the approach of $\overline{N_C(t)}$ to the half-filling value in the steady-state and high-D limits: in a given time interval, electrons have an equal probability of tunneling from the α lead onto the molecule or in the opposite direction due to the random flipping of the sign on the potential gradient, so their probability of occupying the molecular region must be $\frac{1}{2}$. In addition, this nonlinear to linear transition contradicts another key claim of Ref. [31], where it was stated that no change in the shape of the I-V characteristic results from the fluctuating level, except that the amplitude of the current signal is suppressed. To provide some physical insight into this behavior, we plot in Fig. 4(b) the I-V characteristics of the same molecular chain system with the fluctuation parameter kept fixed at $D = 0.1$, and we instead vary k_BT. Interestingly, this case leads to qualitatively similar results to Fig. 4(a), in that the current plotted appears not only to have very similar absolute values, but it also approaches linearity. As discussed in Sec. III C for both dynamical and static modes of the current, the effect of raising the magnitude of the fluctuations is physically similar to raising the temperature throughout the system, explaining the classical behavior at large values of D.

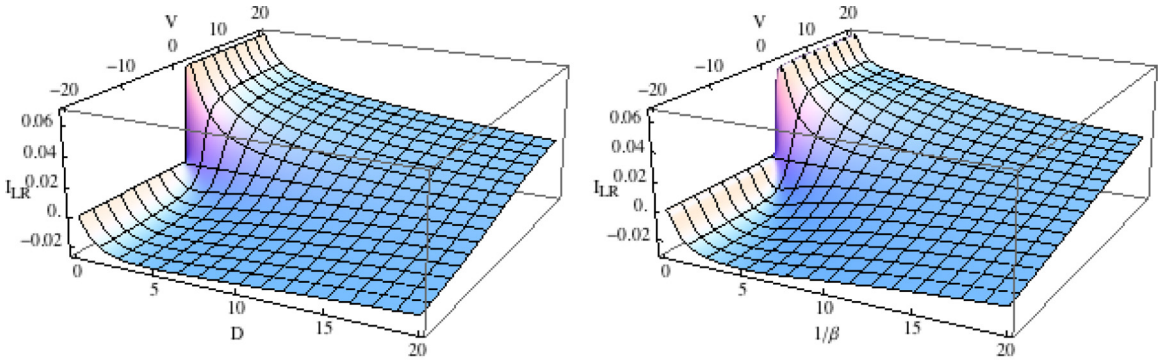


FIG. 4. (a) The symmetrized current as a function of voltage V and fluctuation D, with $k_BT = 0.1$, $V_R = 0$, $\Gamma_{11} = 0.5$, $\Gamma_{55} = 0.5$, $E = 1$, $\lambda = 0.1$. (b) The current in the left lead as a function of V and k_BT, with $D = 0.1$ and all other parameters as in (a).

One might intuitively think that the loss of coherence due to increasing fluctuations in the bias/molecular energies always tends to weaken the current signal. However, when systems possess some sort of activation threshold for a transport process, and a nonlinear dependence on the input signal [95], it is possible for a noisy environment to actually enhance the output signal, in a phenomenon known as *stochastic resonance* [13–15,17]. Notice in Figs. 4(a) and 4(b) that for $V > 1$, the current is always decreasing with D, whereas when $V < 1$, the current possesses a negative maximum for a particular value of D before approaching zero. In the latter case, we see that the current is a nonmonotonic function of D, as it approaches a negative resonant peak for a particular value of D, before decaying to zero. This behavior was seen for a single-level system in Ref. [29] and is also similar to results obtained for the Langevin dynamics of Brownian particles in the asymmetric problems discussed in Sec. III C 2 [7,8,12,96]. We emphasize that whereas the resonance of this Brownian particle occurs in "noise rectifiers" with zero applied bias, we are instead discussing the effects of noise on a system with a nonzero average bias. One can interpret the stochastic resonance in Fig. 4 either in terms of the fluctuating bias or in terms of fluctuating levels. When $V > 1$, the molecular wire energies are always located within the $[V_L, V_R]$ transport window, whereas for $V < 1$, E is always above this window. Taking the bias to fluctuate, one should have in mind a picture of the system where increasing D causes the entire bias window to fluctuate until it overlaps with the molecular energy levels, at which point the transport is enhanced. If the fluctuations are located in the molecular levels, a qualitative interpretation of the resonance derives from the effective broadening of the spectral density of states due to a modified level width [note, however, that Eq. (52) is not strictly valid in this multilevel system as Γ_L is not proportional to Γ_R] [24,29].

In Fig. 5(a), we plot for $\tau_c = 0$ the bias dependence of the conductance

$$G(V; D, \omega_c) \equiv \frac{\partial \overline{I_{LR}}(t \to \infty)}{\partial V} \tag{65}$$

obtained from the long-time limit of $\overline{I_{LR}(t)}$ for the same parameters considered in Fig. 4(a). We see (as observed in Ref. [27]) that the conductance behaves similarly to the transmission function for this system, with a central peak at $V_L = 1$, because at this point the chain energy E overlaps with the bias window. This peak then decays with increasing D, and in understanding the high-D limit it is useful to once again consider the symmetric single-level system of Sec. III C 1. In this model, one can use Eq. (64) to show that, for white noise with a large fluctuation magnitude, the zero-temperature effective resistance $R = G^{-1}$ is given by the constant

$$R = \frac{\pi(\Gamma + 2D)}{\Gamma}. \tag{66}$$

The physics when D is large in our theory is therefore qualitatively similar to the physics of the Nyquist theorem, where R scales linearly with D. However, the most interesting feature of Fig. 5(a) is the existence of a D-dependent resonant peak occurring for $D \sim 1$ at all voltages far from the main resonance. This conductance illustrates that the fluctuations have two effects on the transport, which compete with each other in enhancing/destroying the current signal. The main peak always decreases with increasing D, as this defines the bias at which resonant tunneling is enabled, and increasing the fluctuations broadens the energy levels involved in this quantum process. To illustrate the basic mechanism here, in Fig. 5(b) we plot $G(V; D, \omega_c \to \infty)$ for $V_R = 2$ (dashed lines) beside the conductance for $V_R = 0$ (solid lines) in the molecular wire system. This exchanges the positions of V_R and E without altering the magnitude of $|E - V_R|$. Hence, the position of the main conductance peak is shifted to $V = -1$, but at large V the conductance is independent of the bias, and is instead enhanced at an intermediate value of D (red curves). This value of D corresponds to an optimal spread in energy levels achieved at the point where they overlap with the transport window, without being so large that there is a complete loss of phase in the transport (i.e., when a very small statistical weight is assigned to resonant energies) [24]. In Fig. 5(c), the D dependence of the conductance at $V = 10$ is shown for different values of the gap $|E - V_R|$. The resonant peak occurs when $D \sim |E - V_R|$, i.e., the noise provides the

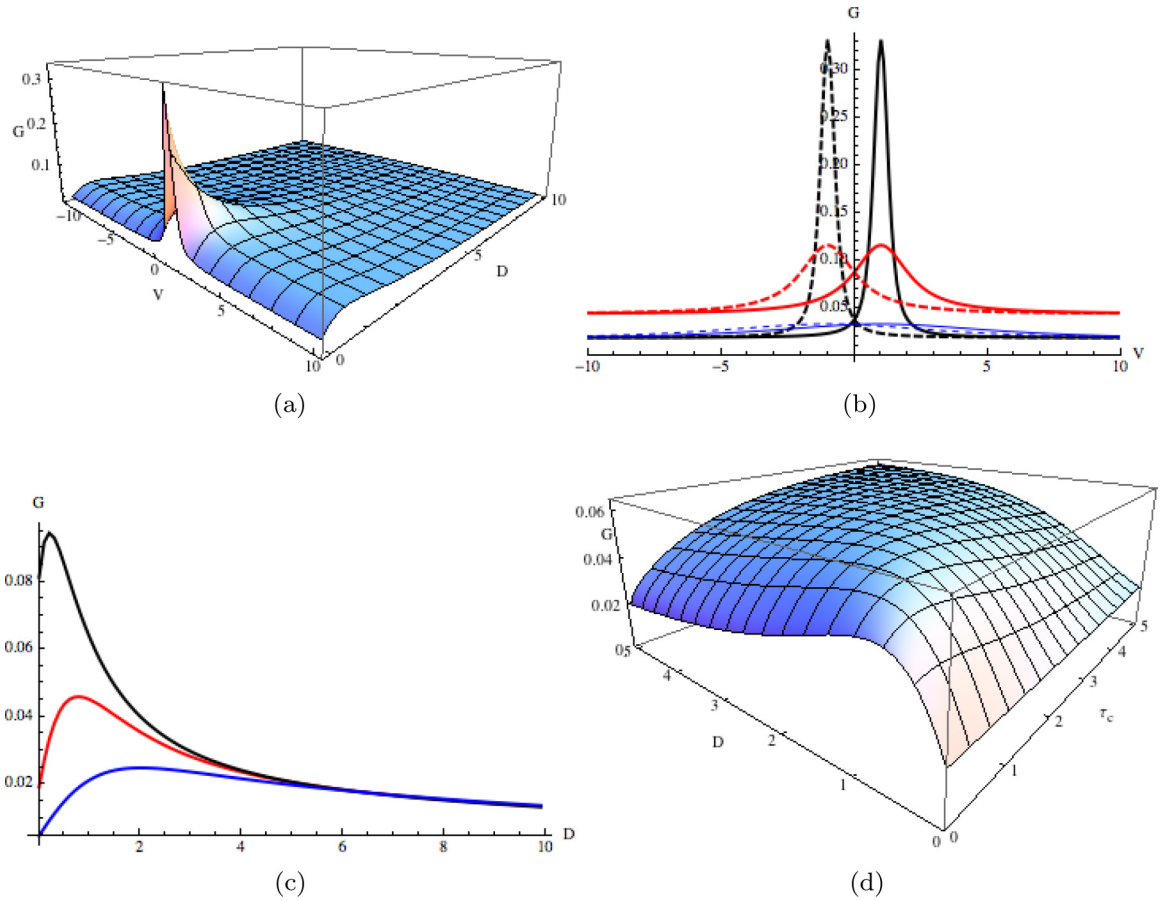


FIG. 5. (a) $G(V; D, \omega_c \to \infty)$ at $V_R = 0$, varying V_L. (b) G-V characteristics at $D = 0$ (black), $D = 1$ (red), $D = 5$ (blue) for $V_R = 0$ (full line) and $V_R = 2$ (dashed line). (c) D dependence of the conductance at $V = 10$, for $|E - V_R| = 0.5$ (black), $|E - V_R| = 1$ (red), and $|E - V_R| = 2$ (blue). (d) $G(V; D, \omega_c \to \infty)$ as a function of both D and τ_c at $V_L = 10$, $V_R = 0$. All plots use the parameters $k_B T = 0.1$, $\Gamma_{11} = 0.5$, $\Gamma_{55} = 0.5$, $E = 1$, $\lambda = 0.1$.

extra energy required for the molecular wire to enter the transport window. This may have applications in devices where resonant tunneling is not viable in practice, and the value of the voltage can only be controlled to lie within a certain range. Such devices may be tuned so that their conductance is stochastically enhanced for most values of the potential difference. Finally, in Fig. 5(d) we plot for the same parameters as in Fig. 5(a) the $V = 10$ conductance as a function of D and τ_c. In the limit $\tau_c \to 0$, the white noise conductance shown in Fig. 5(c) is recovered, with the resonance at $D \sim |E - V_R|$. As τ_c is increased, this resonance is shifted to a value that is greater than $|E - V_R|$, and the rate of decay with increasing D is slowed down in behavior that is reminiscent of the effect of color noise on the transmission function, as illustrated above in Fig. 2(b). In the quasistatic limit of large τ_c, the conductance decays to its $D = 0$ value, as taking $\tau_c \to \infty$ is equivalent to the zero D (frozen bias) limit in Eq. (40). However, when the ratio $D/\tau_c \sim 1$, the rate of decay to the frozen bias limit with increasing τ_c is slowed down, indicating that there is competition between very strong fluctuations and increasing correlation time in the quasistatic regime. This is also apparent from the general Eq. (48), as increasing D tends to cause spreading in the effective transmission whereas increasing τ_c has the opposite effect. This behavior in the conductance is similar to that observed in Ref. [69] for the current through a ratchet driven by fluctuations with the same correlation function as Eq. (36).

V. CONCLUSIONS

In this paper, we showed how to calculate the current through a molecular multiterminal junction due to arbitrary time dependence of the applied bias and an arbitrary homogeneous time-dependent shift of the energy levels of the molecule. First, we showed that the effect of the time-fluctuating molecular levels can be incorporated into the time-dependent bias on the leads of the junction, and hence both effects can be treated on the same mathematical footing. Then, we assumed that either the bias or molecular energies fluctuate in time around some time-constant values with a correlation function given by a single exponential time-decaying function corresponding to a colored noise with the strength D and decaying time τ_c. Under the $\tau_c \to 0$ limit, this noise becomes the white one. Hence, an exact analytical formula has been worked out for the current averaged with respect to this colored (white) noise at all times. Simplified analytical expressions have been worked out in each case (white and colored noise, for long and transient times) which enable straightforward implementation for realistic systems instead of restricting ourselves to single-level molecules. Compared with numerical

approaches to this problem, which must average across many realizations of the stochastic bias, our method provides a massive computational speedup. It will therefore provide an exact benchmark and source of ideas for the qualitative effects of noise on transport through interacting systems, or systems that go beyond the WBLA.

In the long-time limit, the current resulting from a noisy time dependence has the LB form, and from this an exact formal relation was derived between the conductance, the temperature, and the fluctuation strength, which we interpret as a quantum analog to the classical Nyquist theorem relating the electrical resistance of a conductor to the temperature and the strength of the bias fluctuations. We have also discussed a number of claims made in the literature [31] concerning the long-time behavior of the current in the junction due to initial fluctuations of the molecular levels. We find that, at least within the model considered, both the initial preparation of the system and initial bias (or energy levels) fluctuations do not affect the long-time behavior of the current, i.e., our equations do satisfy the memory-loss theorem [56]. Consequently, we were able to prove the claims made in Ref. [31] to be false.

Analytic results, as well as the results of our numerical calculations, performed on a simple five-site atomic chain bridging two electrodes, show that the current-voltage characteristics of our five-atom system transforms from being nonlinear at small D to a linear at large D, something which may have implications for nanodevices. We find that for very large D the conductance is suppressed, as would be expected from the classical Nyquist theorem. However, there exist intermediate values of D at which the conductance may actually be enhanced, due to a finite-energy threshold that needs to be crossed for electronic states to enter the transport window. This "stochastic resonance" occurs due to a tradeoff between quantum coherence and classical noise, although similar physics can be seen in the noise-assisted transport of Brownian particles in spatially asymmetric systems.

A further area for investigation is that of driven noisy systems, which have attracted attention recently in the context of quantum pumps created with stochastically deformable molecules [97]. With our formalism we are able to study the interplay of ac driving frequencies with the inverse correlation time and fluctuation strength in an analytically exact way, combining approaches from [55] and from this paper. The stochastic resonance effect was initially studied in driven systems [13,14], and we anticipate the appearance of frequency- and amplitude-dependent resonances in the transport for different values of τ_c and D, in similar fashion to studies which add a driving term to the classical Langevin equation [12,17,19,21–23]. Finally, we have assumed that the fluctuations in each lead are of the same nature, i.e., that the fluctuation magnitude D and its decay time τ_c are independent of the lead index α. However, the formalism developed above can be easily extended to the treatment of transport caused by asymmetric fluctuations through the introduction of lead indices on D and τ_c.

ACKNOWLEDGMENTS

We are grateful to G. Stefanucci for useful discussions. M.R. was supported through a studentship in the Centre for Doctoral Training on Theory and Simulation of Materials at Imperial College funded by the Engineering and Physical Sciences Research Council under Grant No. EP/G036888/1.

APPENDIX A: LINE INTEGRAL FOR THE GREATER GREEN'S FUNCTION

We first note that the Hamiltonian for the vertical part of the contour is identical to that used in Ref. [54], and so the Matsubara components of the central region Green's function specified by the Hamiltonian in Eq. (8) has already been published there. Using the expression for the retarded self-energy from Ref. [54], the equation of motion for the right Green's function component is manipulated into

$$\left[i\frac{d}{dt_1} - \tilde{\mathbf{h}}^{\mathrm{eff}}\right]\mathbf{G}^{\urcorner}(t_1,\tau_2) = [\Sigma^{\urcorner} \star \mathbf{G}^{M}]_{(t_1,\tau_2)} + V_C(t_1)\mathbf{G}^{\urcorner}(t_1,t_2), \tag{A1}$$

where "$\star$" denotes an integral taken along the vertical part of the contour, and all matrices in bold type are defined in the CC matrix block. Equation (A1) can be solved if one makes the substitution

$$\mathbf{G}^{\urcorner}(t_1,\tau_2) \equiv e^{-i\tilde{\mathbf{h}}^{\mathrm{eff}}(t_1-t_0)}e^{-i\varphi_C(t_1,t_0)}\tilde{\mathbf{G}}^{\urcorner}(t_1,\tau_2). \tag{A2}$$

We can therefore obtain the following equation for the reduced object $\tilde{\mathbf{G}}^{\urcorner}(t_1,\tau_2)$:

$$\frac{d\tilde{\mathbf{G}}^{\urcorner}(t_1,\tau_2)}{dt_1} = -ie^{i\tilde{\mathbf{h}}^{\mathrm{eff}}(t_1-t_0)}e^{i\varphi_C(t_1,t_0)}[\Sigma^{\urcorner} \star \mathbf{G}^{M}]_{(t_1,\tau_2)},$$

which is solved by taking into account the appropriate boundary condition $\tilde{\mathbf{G}}^{\urcorner}(t_0,\tau_2) = \mathbf{G}^{\urcorner}(t_0,\tau_2) = \mathbf{G}^{M}(0^+,\tau_2)$:

$$\mathbf{G}^{\urcorner}(t_1,\tau_2) = e^{-i\tilde{\mathbf{h}}^{\mathrm{eff}}(t_1-t_0)}e^{-i\varphi_C(t_1,t_0)}\left[\mathbf{G}^{M}(0^+,\tau_2) - i\int_{t_0}^{t_1} d\bar{t}\, e^{i\tilde{\mathbf{h}}^{\mathrm{eff}}(\bar{t}-t_0)}e^{i\varphi_C(\bar{t},t_0)}[\Sigma^{\urcorner} \star \mathbf{G}^{M}]_{(\bar{t},\tau_2)}\right]. \tag{A3}$$

Similarly, the left component is given by

$$\mathbf{G}^{\ulcorner}(\tau_1,t_2) = \left[\mathbf{G}^{M}(\tau_1,0^+) + i\int_{t_0}^{t_2} d\bar{t}[\mathbf{G}^{M} \star \Sigma^{\ulcorner}]_{(\tau_1,\bar{t})}e^{-i(\tilde{\mathbf{h}}^{\mathrm{eff}})^{\dagger}(\bar{t}-t_0)}e^{-i\varphi_C(\bar{t},t_0)}\right]e^{i(\tilde{\mathbf{h}}^{\mathrm{eff}})^{\dagger}(t_2-t_0)}e^{i\varphi_C(t_2,t_0)}. \tag{A4}$$

Note that the obtained expressions contain exponential functions of the matrix $\widetilde{\mathbf{h}}^{\rm eff}$, and 0^+ is slightly larger than 0. Formally, Eqs. (A3) and (A4) for the right and left Green's functions in terms of different components are identical to those given in [42] for the constant bias switch-on case, with the addition of the φ_C phase factors. For completeness, we add that the Matsubara component of the Green's function is unchanged from the expression given in [42,55] (note that $\mathbf{h}^{\rm eff}$ is defined without the tilde):

$$\mathbf{G}^M(\tau_1,\tau_2) = \frac{i}{\beta}\sum_q e^{-\omega_q(\tau_1-\tau_2)}\mathbf{G}^M(\omega_q) \equiv \frac{i}{\beta}\sum_q e^{-\omega_q(\tau_1-\tau_2)}\begin{cases}[(\omega_q+\mu)\mathbf{1}_{CC}-\mathbf{h}^{\rm eff}]^{-1}, & {\rm Im}(\omega_q)>0\\ [(\omega_q+\mu)\mathbf{1}_{CC}-(\mathbf{h}^{\rm eff})^\dagger]^{-1}, & {\rm Im}(\omega_q)<0.\end{cases} \tag{A5}$$

When we project Eq. (12) and its complex conjugate onto the greater component, using appropriate Langreth rules and the known expression for the retarded self-energy, we obtain the following equations of motion for the greater Green's function:

$$\left[i\frac{d}{dt_1}-\widetilde{\mathbf{h}}^{\rm eff}\right]\mathbf{G}^>(t_1,t_2) = [\Sigma^>\cdot\mathbf{G}^a+\Sigma^\urcorner\star\mathbf{G}^\ulcorner]_{(t_1,t_2)}+V_C(t_1)\mathbf{G}^>(t_1,t_2), \tag{A6}$$

$$\mathbf{G}^>(t_1,t_2)\left[-i\frac{d}{dt_2}-\widetilde{\mathbf{h}}^{\rm eff\dagger}\right] = [\mathbf{G}^r\cdot\Sigma^>+\mathbf{G}^\urcorner\star\Sigma]_{(t_1,t_2)}+\mathbf{G}^>(t_1,t_2)V_C(t_2). \tag{A7}$$

Here, the "centerdot" denotes an integral taken along the horizontal part of the contour. We now look to put the WBLA Kadanoff-Baym equations for the greater Green's functions into a form suitable for the integration. This is done by introducing the "tilded" greater Green's function $\widetilde{\mathbf{G}}^>(t_1,t_2)$ via the transformation

$$\mathbf{G}^>(t_1,t_2) \equiv e^{-i\widetilde{\mathbf{h}}^{\rm eff}(t_1-t_0)}\widetilde{\mathbf{G}}^>(t_1,t_2)e^{i\widetilde{\mathbf{h}}^{\dagger{\rm eff}}(t_2-t_0)}e^{-i\varphi_C(t_1,t_2)}. \tag{A8}$$

This is substituted into the WBLA Kadanoff-Baym equations (A6) and (A7) to finally obtain integrable first-order differential equations for $\widetilde{\mathbf{G}}^>_{CC}(t_1,t_2)$:

$$\frac{\partial\widetilde{\mathbf{G}}^>(t_1,t_2)}{\partial t_1} = -ie^{i\widetilde{\mathbf{h}}^{\rm eff}(t_1-t_0)}[\Sigma^>\cdot\mathbf{G}^a+\Sigma^\urcorner\star\mathbf{G}^\ulcorner]_{(t_1,t_2)}e^{-i\widetilde{\mathbf{h}}^{\dagger{\rm eff}}(t_2-t_0)}e^{i\varphi_C(t_1,t_2)}, \tag{A9}$$

$$\frac{\partial\widetilde{\mathbf{G}}^>(t_1,t_2)}{\partial t_2} = ie^{i\widetilde{\mathbf{h}}^{\rm eff}(t_1-t_0)}[\mathbf{G}^r\cdot\Sigma^>+\mathbf{G}^\urcorner\star\Sigma^\ulcorner]_{(t_1,t_2)}e^{-i\widetilde{\mathbf{h}}^{\dagger{\rm eff}}(t_2-t_0)}e^{i\varphi_C(t_1,t_2)}. \tag{A10}$$

The analyticity of the Green's function (proven in Ref. [54]) means that the tilded Green's function is calculated using a line integral along the path $(t_{0+},t_{0-})\longrightarrow(t_{1+},t_{0-})\longrightarrow(t_{1+},t_{2-})$ on the (t_1,t_2) plane, where $t_{0-}=t_0+i0$ is the time t_0 on the upper horizontal part of the contour, while $t_{0+}=t_0-i0$ is the later time lying on the lower horizontal track of the Konstantinov-Perel' contour. Hence, the greater GF can be found from the line integral

$$\begin{aligned}\widetilde{\mathbf{G}}^>(t_1,t_2)-\widetilde{\mathbf{G}}^>(t_{0+},t_{0-}) &= -i\int_{t_0}^{t_1}d\bar{t}\,e^{i\widetilde{\mathbf{h}}^{\rm eff}(\bar{t}-t_0)}[\Sigma^>\cdot\mathbf{G}^a+\Sigma^\urcorner\star\mathbf{G}^\ulcorner]_{(\bar{t}_+,t_{0-})}e^{i\varphi_C(\bar{t},t_0)}\\ &\quad+i\int_{t_0}^{t_2}d\bar{t}\,e^{i\widetilde{\mathbf{h}}^{\rm eff}(t_1-t_0)}[\mathbf{G}^r\cdot\Sigma^>+\mathbf{G}^\urcorner\star\Sigma^\ulcorner]_{(t_{1+},\bar{t}_-)}e^{-i\widetilde{\mathbf{h}}^{\dagger{\rm eff}}(t_2-t_0)}e^{i\varphi_C(t_1,\bar{t})}\equiv\sum_{i=1}^4\mathcal{G}^>_{(4)}.\end{aligned} \tag{A11}$$

To evaluate the boundary condition $\widetilde{\mathbf{G}}^>(t_0,t_0)=\mathbf{G}^M(0^+,0)$, we use the theorem [42]

$$\frac{i}{\beta}\sum_{n=-\infty}^{\infty}Q(\omega_n)e^{-\omega_n 0^+} = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}[1-f(\omega)]e^{-\omega 0^+}[Q(\omega+i0)-Q(\omega-i0)]. \tag{A12}$$

This lets us extract the functional form of the initial condition for the line integral in (A11):

$$\widetilde{\mathbf{G}}^>(t_{0+},t_{0-}) = -i\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}[1-f(\omega-\mu)]\sum_\alpha\mathbf{A}_\alpha(\omega). \tag{A13}$$

Above, we have introduced the spectral function $\mathbf{A}_\alpha(\omega)=\mathbf{G}^r(\omega)\Gamma_\alpha\mathbf{G}^a(\omega)$ for the α lead. We now present some details of the analytic evaluation of the convolution integrals $\mathcal{G}^>_{(i)}$. This derivation is based upon the similar derivation of [42] for the lesser Green's function of a single time, and details for the lesser Green's function can be found in Ref. [54]. There are now four convolution integrals to perform. First, we can see that $\mathcal{G}^>_{(1)}=0$ because

$$[\Sigma^>\cdot\mathbf{G}^a]_{(\bar{t}_+,t_{0-})} = \int_{t_0}^{\bar{t}}d\bar{t}'\,\Sigma^>(\bar{t},\bar{t}')i\theta(t_0-\bar{t}')e^{-i\widetilde{\mathbf{h}}^{\dagger{\rm eff}}(\bar{t}-t_0)}e^{-i\varphi_C(\bar{t},t_0)}=0.$$

Next, we must consider the object $[\Sigma^\urcorner\star\mathbf{G}^\ulcorner]_{(\bar{t}_+,t_{0-})}$. From the exact expressions derived for the right and Matsubara GFs, and the fact that $[\Sigma^\urcorner\star\mathbf{G}^M\star\Sigma^\ulcorner]_{(\bar{t},\bar{t}')}=0$, it quickly follows that

$$[\Sigma^\urcorner\star\mathbf{G}]^\ulcorner_{(\bar{t}_+,t_{0-})} = \frac{i}{\beta}\sum_\alpha\Gamma_\alpha e^{-i\psi_\alpha(\bar{t},t_0)}\sum_{q=-\infty}^{\infty}\int\frac{d\omega}{2\pi}\frac{e^{-i\omega(\bar{t}-t_0)}}{\omega_q-\omega+\mu}\mathbf{G}^M(\omega_q)e^{-\omega_q 0^+}.$$

Using the identity (A12) and doing the resulting contour integrals, one can remove the Matsubara summation

$$[\Sigma^{\ulcorner} \star \mathbf{G}^{\urcorner}]_{(\bar{t}_+,t_{0-})} = -i\sum_{\alpha}\Gamma_{\alpha}e^{-i\psi_{\alpha}(\bar{t},t_0)}\int\frac{d\omega}{2\pi}[1-f(\omega-\mu)]e^{-i\omega(\bar{t}-t_0)}\mathbf{G}^{a}(\omega).$$

The remaining part of the integral taken between t_0 and t_1 is then expressible as

$$\mathcal{G}^{>}_{(2)} = -\sum_{\alpha}\int\frac{d\omega}{2\pi}[1-f(\omega-\mu)]\mathbf{K}_{\alpha}(t_1,t_0;\omega)\Gamma_{\alpha}\mathbf{G}^{a}(\omega),$$

where we have defined the following matrix object for the α lead:

$$\mathbf{K}_{\alpha}(t,t_0;\omega) = \int_{t_0}^{t} d\bar{t}\, e^{-i(\omega\mathbf{1}-\tilde{\mathbf{h}}^{\mathrm{eff}})(\bar{t}-t_0)}e^{i(\varphi_C-\psi_{\alpha})(\bar{t},t_0)}. \tag{A14}$$

Note that this definition of the $\mathbf{K}_{\alpha}$ only differs from that given in [54] by the phase factor $e^{i\varphi_C(\bar{t},t_0)}$ and the modified Hamiltonian $\tilde{\mathbf{h}}$. The third convolution integral is obtained from $\mathbf{G}^{r}\cdot\Sigma^{>}$, which is easily evaluated using Eq. (19) and the self-energy component from Ref. [54]:

$$\mathcal{G}^{>}_{(3)} = -i\sum_{\alpha}\int\frac{d\omega}{2\pi}[1-f(\omega-\mu)]\mathbf{K}_{\alpha}(t_1,t_0;\omega)\Gamma_{\alpha}\mathbf{K}^{\dagger}_{\alpha}(t_2,t_0;\omega).$$

We have in the final term the vertical contour convolution

$$[\mathbf{G}^{\ulcorner}\star\Sigma^{\urcorner}]_{(t_{1+},\bar{t}_-)} = e^{-i\tilde{\mathbf{h}}^{\mathrm{eff}}(t_1-t_0)}e^{-i\varphi_C(t_1,t_0)}\left[[\mathbf{G}^{M}\star\Sigma^{\urcorner}]_{(0_+,\bar{t}_-)} - i\int_{t_0}^{t_1}d\bar{t}'e^{i\tilde{\mathbf{h}}^{\mathrm{eff}}(\bar{t}-t_0)}e^{i\varphi_C(\bar{t},t_0)}[\Sigma^{\ulcorner}\star\mathbf{G}^{M}\star\Sigma^{\urcorner}]_{(\bar{t}'_+,\bar{t}_-)}\right].$$

Using similar techniques to those in [42,54], and making use of the identity (A12), we obtain

$$\mathcal{G}^{>}_{(4)} = \sum_{\alpha}\int\frac{d\omega}{2\pi}[1-f(\omega-\mu)]\mathbf{G}^{r}(\omega)\Gamma_{\alpha}\mathbf{K}^{\dagger}_{\alpha}(t_2,t_0;\omega).$$

Collecting all the terms together now, we map back from the transformation (A8) and use the initial condition (A13) to get the greater GF:

$$\begin{aligned}\mathbf{G}^{>}(t_1,t_2) = -e^{-i\varphi_C(t_1,t_0)}e^{-i\tilde{\mathbf{h}}^{\mathrm{eff}}(t_1-t_0)}\sum_{\alpha}\int\frac{d\omega}{2\pi}[1-f(\omega-\mu)]\sum_{\alpha}\{&\mathbf{K}_{\alpha}(t_1,t_0;\omega)\Gamma_{\alpha}\mathbf{G}^{a}(\omega) - \mathbf{G}^{r}(\omega)\Gamma_{\alpha}\mathbf{K}^{\dagger}_{\alpha}(t_2,t_0;\omega)\\ &+i[\mathbf{K}_{\alpha}(t_1,t_0;\omega)\Gamma_{\alpha}\mathbf{K}^{\dagger}_{\alpha}(t_2,t_0;\omega)+\mathbf{A}_{\alpha}(\omega)]\}e^{i\tilde{\mathbf{h}}^{\dagger\mathrm{eff}}(t_2-t_0)}e^{i\varphi_C(t_2,t_0)}.\end{aligned} \tag{A15}$$

A similar formula to Eq. (A15) can be found for the lesser Green's function, but we can represent it more compactly than in previously published work if we introduce the matrix $\mathbf{S}_{\alpha}$ defined in Eq. (22). It is then seen that the greater and lesser Green's functions can be written as in Eq. (23), and all transport quantities can be represented in terms of the $\mathbf{S}_{\alpha}$.

APPENDIX B: QUASISTATIC FORMULAS

To project the formula (39) onto the left/right eigenbasis, we insert (40) in all places where the phase average appears and make use of the following idempotency relation:

$$\sum_{j}\frac{|\varphi^{R}_{j}\rangle\langle\varphi^{L}_{j}|}{\langle\varphi^{L}_{j}|\varphi^{R}_{j}\rangle} = \mathbf{I} = \sum_{j}\frac{|\varphi^{L}_{j}\rangle\langle\varphi^{R}_{j}|}{\langle\varphi^{R}_{j}|\varphi^{L}_{j}\rangle}. \tag{B1}$$

This identity is used twice in the part containing the double-time integral in the current formula (39), and once everywhere else, to give for the bias-averaged current

$$\begin{aligned}\overline{I_{\alpha}(t)} = \frac{1}{\pi}\int d\omega\, f(\omega-V_{\alpha}-\mu)\mathrm{Re}\Bigg(&\sum_{j}\frac{\langle\varphi^{L}_{j}|\Gamma_{\alpha}|\varphi^{R}_{j}\rangle}{\langle\varphi^{L}_{j}|\varphi^{R}_{j}\rangle}\Bigg\{ie^{-\frac{D\omega_c(t-t_0)^2}{2}}\frac{e^{i(\omega-\bar{\varepsilon}_j)(t-t_0)}}{\omega-V_{\alpha}-\bar{\varepsilon}_j}\\ &+\sqrt{\frac{\pi}{2D\omega_c}}e^{-\frac{(\omega-\bar{\varepsilon}_j)^2}{2D\omega_c}}\left[\mathrm{erf}\left(\sqrt{\frac{D\omega_c}{2}}(t-t_0)-i\frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi\,D\omega_c}}\right)+\mathrm{erf}\left(i\frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi\,D\omega_c}}\right)\right]\Bigg\}\Bigg)\\ -\frac{1}{\pi}\int d\omega\sum_{\beta,j,k}&f(\omega-V_{\beta}-\mu)\frac{\langle\varphi^{R}_{k}|\Gamma_{\alpha}|\varphi^{R}_{j}\rangle\langle\varphi^{L}_{j}|\Gamma_{\gamma}|\varphi^{L}_{k}\rangle}{\langle\varphi^{L}_{j}|\varphi^{R}_{j}\rangle\langle\varphi^{R}_{k}|\varphi^{L}_{k}\rangle}\left(\frac{e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}^{*}_{k})(t-t_0)}}{(\omega-\bar{\varepsilon}_j)(\omega-\bar{\varepsilon}^{*}_{k})}\right.\end{aligned}$$

$$+\sqrt{\frac{\pi}{2D\omega_c}}\left\{i\frac{e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}e^{-\frac{(\omega-\varepsilon_j)^2}{2D\omega_c}}}{\omega-V_\gamma-\bar{\varepsilon}_k^*}\left[\mathrm{erf}\left(\sqrt{\frac{D\omega_c}{2}}(t-t_0)+i\frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right)-\mathrm{erf}\left(i\frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right)\right]+\text{c.c.}_{j\leftrightarrow k}\right\}$$
$$+e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}\int_0^{t-t_0}dx\int_0^{t-t_0}dy\,e^{-i(\omega-\bar{\varepsilon}_j)x}e^{i(\omega-\bar{\varepsilon}_k^*)y}e^{-\frac{D\omega_c}{2}(x-y)^2}\Bigg) \tag{B2}$$

Here, we use the notation c.c.$_{j\leftrightarrow k}$ to denote the complex conjugation of the preceding term with indices j and k exchanged.

The double integral on the final line can be removed with the aid of the mathematical identity

$$\int_0^A dx\,\mathrm{erf}[B(x+C)]e^{iDx}=\frac{1}{iD}\left\{e^{iDA}\mathrm{erf}[B(A+C)]-\mathrm{erf}(BC)-e^{-iDC}e^{-\frac{D^2}{4B^2}}\left[\mathrm{erf}\left(B(A+C)-\frac{iD}{2B}\right)-\mathrm{erf}\left(BC-\frac{iD}{2B}\right)\right]\right\}.$$

Following some tedious but mathematically trivial manipulations, one finally ends with a closed expression for this double integral. To simplify the resulting formula, we note that because $\Gamma=i(\mathbf{h}^{\mathrm{eff}}-\mathbf{h}^{\mathrm{eff}\dagger})$, the identity

$$\langle\varphi_j^L|\Gamma_\alpha|\varphi_k^R\rangle=i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)\langle\varphi_j^L|\varphi_k^R\rangle-\sum_{\gamma\neq\alpha}\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^R\rangle$$

must be valid and so the following relation can be proven:

$$f_\alpha\sum_j\frac{\langle\varphi_j^L|\Gamma_\alpha|\varphi_j^R\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle}c_j-\sum_\gamma f_\gamma\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)}c_j=\sum_{\gamma\neq\alpha}[f_\alpha-f_\gamma]\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)}c_j. \tag{B3}$$

In this expression, f_γ can be any function of parameters which depend on the lead index γ. This leads us finally to reexpress (B2) as a sum of a term that decays to zero asymptotically and a term which is of the LB type:

$$\begin{aligned}\overline{I_\alpha(t)}\;=&\;\frac{1}{\pi}\sum_{\gamma\neq\alpha}[f(\omega-V_\alpha-\mu)-f(\omega-V_\gamma-\mu)]T_{\gamma\alpha}(\omega,t-t_0)\\
&+\frac{1}{\pi}\mathrm{Re}\int d\omega\,f(\omega-V_\alpha-\mu)\Bigg(\sum_j\frac{\langle\varphi_j^L|\Gamma_\alpha|\varphi_j^R\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle}ie^{-\frac{D\omega_c}{2}(t-t_0)^2}\frac{e^{i(\omega-\bar{\varepsilon}_j)(t-t_0)}}{\omega-V_\alpha-\bar{\varepsilon}_j}\\
&-\sum_{j,k,\gamma}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle}\Bigg\{\frac{e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}}{(\omega-\bar{\varepsilon}_j)(\omega-\bar{\varepsilon}_k^*)}\\
&+i\sqrt{\frac{\pi}{2D\omega_c}}\frac{e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}e^{-\frac{(\omega-\bar{\varepsilon}_j)^2}{2D\omega_c}}(\bar{\varepsilon}_j-\omega+V_\gamma)}{(\omega-V_\gamma-\bar{\varepsilon}_k^*)(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)}\left[\mathrm{erf}\left(\sqrt{\frac{D\omega_c}{2}}(t-t_0)+i\frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right)-\mathrm{erf}\left(i\frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right)\right]\Bigg\}\Bigg),\end{aligned} \tag{B4}$$

where we make the definition of the time-dependent transmission probability:

$$\begin{aligned}T_{\gamma\alpha}(\omega,t-t_0)=&\sqrt{\frac{\pi}{2D\omega_c}}\sum_{j,k}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)}\\
&\times\left\{e^{-\frac{(\omega-\bar{\varepsilon}_j)^2}{2D\omega_c}}\left[\mathrm{erf}\left(\sqrt{\frac{D\omega_c}{2}}(t-t_0)-i\frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right)+\mathrm{erf}\left(i\frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right)\right]+\text{c.c.}_{j\leftrightarrow k}\right\}.\end{aligned} \tag{B5}$$

The LB term therefore depends on $t-t_0$ at finite times but has an asymptotically finite value given by Eq. (43), while all other modes of the current vanish asymptotically. It should also be noted that in the long-time limit, all the dependence on the lead index γ goes into the Fermi function and level width matrix.

APPENDIX C: EXACT TIME-DEPENDENT CURRENT FOR COLORED NOISE BIAS

When deriving the bias-averaged current for arbitrary values of τ_c, one inserts (46) into (39), and evaluates the subsequent formula in the left/right eigenbasis as was done for Eq. (B4). Once again using the relation (B3), it is possible to split the formula for the time-dependent current into a part that converges to a fixed value and a part that decays to zero with increasing $t-t_0$:

$$\begin{aligned}\overline{I_\alpha(t)}=&\frac{1}{\pi}\sum_{\gamma\neq\alpha}\int d\omega[f(\omega-V_\alpha-\mu)-f(\omega-V_\gamma-\mu)]T_{\gamma\alpha}(\omega,D,\omega_c)\\
&+\frac{1}{\pi}\sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n\sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}\int d\omega\,f(\omega-\mu)\Bigg\{2\,\mathrm{Re}\left[\sum_j\frac{\langle\varphi_j^L|\Gamma_\alpha|\varphi_j^R\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle}i\frac{e^{i[\omega+V_\alpha-\varepsilon_j+i(D+m\omega)](t-t_0)}[V_\alpha+i(D+m\omega_c)]}{(\omega-\bar{\varepsilon}_j)[\omega+V_\alpha-\bar{\varepsilon}_j+i(D+m\omega_c)]}\right]\end{aligned}$$

$$-\sum_{j,k,\gamma}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle}\Bigg[\frac{e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}}{(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)}\left(\frac{\delta_{n0}}{\omega-\bar{\varepsilon}_j}-\frac{1}{[\omega+V_\gamma-\bar{\varepsilon}_j+i(D+m\omega_c)]}\right)$$
$$+\frac{[e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}-e^{i[\omega+V_\gamma-\varepsilon_j+i(D+m\omega)](t-t_0)}]}{[\omega+V_\gamma-\bar{\varepsilon}_k^*+i(D+m\omega_c)]}\left(\frac{1}{\omega-\bar{\varepsilon}_j}-\frac{1}{[\omega+V_\gamma-\bar{\varepsilon}_j+i(D+m\omega_c)]}\right)+\text{c.c.}_{j\leftrightarrow k}\Bigg]\Bigg\}, \tag{C1}$$

where $T_{\beta\alpha}(\omega,D,\omega_c)$ is given by Eq. (48).

For numerical implementations, it is useful to replace the frequency integrals in Eq. (C1) with summations. This can be done by inserting Eq. (53) into the current formula and removing all time integrals explicitly, as discussed in Sec. III C 2. One can use either the Padé or Matsubara expansions to do this. If the Matsubara expansion is used, all integrals can be analytically carried out and the resulting summations expressed in terms of special functions. The first of these is the so-called *Hurwitz-Lerch transcendent* Φ [98]:

$$\Phi(z,s,a)\equiv\sum_{n=0}^{\infty}\frac{z^n}{(n+a)^s}. \tag{C2}$$

This arises from Eq. (C1) via integrals over terms of the form $e^{i\omega\tau}/(\omega-z)$, where z is a complex valued pole. We also need the *digamma function* Ψ, defined as the logarithmic derivative of the complex gamma function [58]. The difference of two digamma functions is equal to the infinite series which arises from terms with a double-pole structure:

$$\frac{\Psi(z_1)-\Psi(z_2)}{z_1-z_2}=\sum_{n=0}^{\infty}\frac{1}{(n+z_1)(n+z_2)}. \tag{C3}$$

We introduce the following compact notation:

$$\bar{\Phi}(\beta,\tau,z)\equiv\exp\left(-\frac{\pi\tau}{\beta}\right)\Phi\left(e^{-\frac{2\pi\tau}{\beta}},1,\frac{1}{2}+\frac{\beta z}{2i\pi}\right). \tag{C4}$$

The average current can then be expressed entirely in terms of embedded summations over special functions:

$$\overline{I_\alpha(t)}=\frac{2}{\pi}\text{Re}\sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n\sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}\sum_j\Bigg\{i\frac{\langle\varphi_j^L|\Gamma_\alpha|\varphi_j^R\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle}\Bigg[\Psi\left(\frac{1}{2}-\frac{\beta}{2i\pi}[\bar{\varepsilon}_j-\mu-V_\alpha-i(D+m\omega_c)]\right)$$
$$+e^{-i[\bar{\varepsilon}_j-\mu-V_\alpha-i(D+m\omega_c)](t-t_0)}(\bar{\Phi}\{\beta,t-t_0,-[\bar{\varepsilon}_j-\mu-V_\alpha-i(D+m\omega_c)]\}-\bar{\Phi}[\beta,t-t_0,-(\bar{\varepsilon}_j-\mu)])\Bigg]$$
$$-\sum_{k,\gamma}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle}\Bigg[\frac{\delta_{n0}e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}}{\bar{\varepsilon}_k^*-\bar{\varepsilon}_j}\Psi\left(\frac{1}{2}+\frac{\beta}{2i\pi}(\bar{\varepsilon}_k^*-\mu)\right)$$
$$+\frac{[e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}-1]}{\bar{\varepsilon}_k^*-\bar{\varepsilon}_j}\Psi\left(\frac{1}{2}-\frac{\beta}{2i\pi}[\bar{\varepsilon}_j-\mu-V_\gamma-i(D+m\omega_c)]\right)$$
$$+\frac{e^{-i[\bar{\varepsilon}_j-\mu-V_\gamma-i(D+m\omega_c)](t-t_0)}}{\bar{\varepsilon}_k^*-\bar{\varepsilon}_j-V_\gamma-i(D+m\omega_c)}[\bar{\Phi}[\beta,t-t_0,-(\bar{\varepsilon}_j-\mu)]-\bar{\Phi}\{\beta,t-t_0,-[\bar{\varepsilon}_k^*-\mu-V_\gamma-i(D+m\omega_c)]\}]$$
$$+\frac{e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}}{\bar{\varepsilon}_k^*-\bar{\varepsilon}_j-V_\gamma-i(D+m\omega_c)}\left[\Psi\left(\frac{1}{2}-\frac{\beta}{2i\pi}(\bar{\varepsilon}_j-\mu)\right)-\Psi\left(\frac{1}{2}-\frac{\beta}{2i\pi}[\bar{\varepsilon}_k^*-\mu-V_\gamma-i(D+m\omega_c)]\right)\right]$$
$$+\frac{e^{-i[\bar{\varepsilon}_j-\mu-V_\gamma-i(D+m\omega_c)](t-t_0)}}{\bar{\varepsilon}_k^*-\bar{\varepsilon}_j}[\bar{\Phi}\{\beta,t-t_0,-[\bar{\varepsilon}_k^*-\mu-V_\gamma-i(D+m\omega_c)]\}$$
$$-\bar{\Phi}\{\beta,t-t_0,-[\bar{\varepsilon}_j-\mu-V_\gamma-i(D+m\omega_c)]\}]$$
$$+\frac{e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}}{\bar{\varepsilon}_k^*-\bar{\varepsilon}_j}\left[\Psi\left(\frac{1}{2}-\frac{\beta}{2i\pi}[\bar{\varepsilon}_k^*-\mu-V_\gamma-i(D+m\omega_c)]\right)-\Psi\left(\frac{1}{2}-\frac{\beta}{2i\pi}[\bar{\varepsilon}_j-\mu-V_\gamma-i(D+m\omega_c)]\right)\right]\Bigg]\Bigg\} \tag{C5}$$

In the long-time limit, one can use the theorem (B3) to show that (C5) reduces to the following form:

$$\lim_{t_0\to-\infty}\overline{I_\alpha(t)} = \frac{1}{\pi}\sum_{n=0}^{\infty}\left(\frac{D}{\omega_c}\right)^n\sum_{m=0}^{n}\frac{(-1)^m}{(n-m)!m!}\sum_{j,k,\gamma}\frac{\langle\varphi_k^R|\Gamma_\alpha|\varphi_j^R\rangle\langle\varphi_j^L|\Gamma_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)}$$
$$\times\left\{\Psi\left(\frac{1}{2}-\frac{\beta}{2i\pi}[\bar{\varepsilon}_j-\mu-V_\alpha-i(D+m\omega_c)]\right)-\Psi\left(\frac{1}{2}+\frac{\beta}{2i\pi}[\bar{\varepsilon}_k^*-\mu-V_\alpha+i(D+m\omega_c)]\right)\right.$$
$$\left.-\Psi\left(\frac{1}{2}-\frac{\beta}{2i\pi}[\bar{\varepsilon}_j-\mu-V_\gamma-i(D+m\omega_c)]\right)+\Psi\left(\frac{1}{2}+\frac{\beta}{2i\pi}[\bar{\varepsilon}_k^*-\mu-V_\gamma+i(D+m\omega_c)]\right)\right\}. \quad \text{(C6)}$$

It can be easily seen, by inserting the Matsubara poles into the expression for $I_\alpha^{\mathrm{LB}}(D,\omega_c)$, Eq. (54), that it is equivalent to (C6). However, Eq. (C6) allows for a much faster numerical implementation of the asymptotic current average.

[1] J. B. Johnson, Phys. Rev. **32**, 97 (1928).
[2] H. Nyquist, Phys. Rev. **32**, 110 (1928).
[3] N. Pottier, *Nonequilibrium Statistical Physics: Linear Irreversible Processes* (Oxford University Press, Oxford, 2011).
[4] R. Kubo, Rep. Prog. Phys. **29**, 255 (1966).
[5] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, Oxford, 2001).
[6] L. Kantorovich, Phys. Rev. B **78**, 094304 (2008).
[7] C. R. Doering, W. Horsthemke, and J. Riordan, Phys. Rev. Lett. **72**, 2984 (1994).
[8] M. M. Millonas and M. I. Dykman, Phys. Lett. A **185**, 65 (1994).
[9] J. Łuczka, R. Bartussek, and P. Hänggi, Europhys. Lett. **31**, 431 (1995).
[10] J. Kula, T. Czernik, and J. Łuczka, Phys. Lett. A **214**, 14 (1996).
[11] J. Łuczka, T. Czernik, and P. Hänggi, Phys. Rev. E **56**, 3968 (1997).
[12] J.-h. Li, J. Łuczka, and P. Hänggi, Phys. Rev. E **64**, 011113 (2001).
[13] R. Benzi, A. Sutera, and A. Vulpiani, J. Phys. A: Math. Gen. **14**, 453 (1981).
[14] R. Benzi, A. Sutera, and A. Vulpiani, Tellus **34**, 10 (1982).
[15] L. Gammaitoni, P. Hänggi, P. Jung, and F. Marchesoni, Rev. Mod. Phys. **70**, 223 (1998).
[16] P. Hänggi, G. Schmid, and I. Goychuk, Nova Acta Leopoldina **88**, 17 (2003).
[17] P. Hänggi and F. Marchesoni, Rev. Mod. Phys. **81**, 387 (2009).
[18] P. Langevin, C. R. Acad. Sci. (Paris) **146**, 530 (1908).
[19] P. Jung and P. Hänggi, Europhys. Lett. **8**, 505 (1989).
[20] R. Bartussek, P. Hänggi, B. Lindner, and L. Schimansky-Geier, Phys. D (Amsterdam) **109**, 17 (1997).
[21] C. J. Tessone, H. S. Wio, and P. Hänggi, Phys. Rev. E **62**, 4623 (2000).
[22] M. Borromeo and F. Marchesoni, Europhys. Lett. **72**, 362 (2005).
[23] M. Borromeo and F. Marchesoni, Chaos **15**, 026110 (2005).
[24] M. B. Plenio and S. F. Huelga, New J. Phys. **10**, 113019 (2008).
[25] P. Rebentrost, M. Mohseni, I. Kassal, S. Lloyd, and A. Aspuru-Guzik, New J. Phys. **11**, 033003 (2009).
[26] S. Viciani, M. Lima, M. Bellini, and F. Caruso, Phys. Rev. Lett. **115**, 083601 (2015).
[27] A. I. German, V. A. Kovarskii, and N. F. Perel'man, Zh. Eksp. Teor. Fiz. **106**, 801 (1994) [J. Exp. Theor. Phys. **79**, 439 (1994)].
[28] I. Goychuk and Hänggi, Adv. Phys. **54**, 525 (2005).
[29] A. Croy and U. Saalmann, Phys. Rev. B **80**, 245311 (2009).
[30] B. Popescu, P. B. Woiczikowski, M. Elstner, and U. Kleinekathöfer, Phys. Rev. Lett. **109**, 176802 (2012).
[31] P. Wang, G. Xianlong, and S. Xu, Europhys. Lett. **105**, 37004 (2014).
[32] P. R. Bandaru, C. Daraio, S. Jin, and A. M. Rao, Nat. Mater. **4** 663 (2005).
[33] I. Iñiguez-de-la Torre, T. González, D. Pardo, C. Gardès, Y. Roelens, S. Bollaert, A. Curutchet, C. Gaquiere, and J. Mateos, Semicond. Sci. Technol. **25**, 125013 (2010).
[34] M. Di Ventra and N. D. Lang, Phys. Rev. B **65**, 045402 (2001).
[35] J. A. Fürst, J. Hashemi, T. Markussen, M. Brandbyge, A.-P. Jauho, and R. M. Nieminen, Phys. Rev. B **80**, 035427 (2009).
[36] C. J. O. Verzijl and J. M. Thijssen, J. Chem. Phys. C **116**, 24393 (2012).
[37] C. J. O. Verzijl, J. S. Seldenthuis, and J. M. Thijssen, J. Chem. Phys. **138**, 094102 (2013).
[38] R. Landauer, Philos. Mag. **21**, 863 (1970).
[39] Y. Imry and R. Landauer, Rev. Mod. Phys. **71**, S306 (1999).
[40] Y. M. Blanter and M. Büttiker, Phys. Rep. **336**, 1 (2000).
[41] M. Di Ventra, *Electrical Transport in Nanoscale Systems* (Cambridge University Press, Cambridge, 2008).
[42] G. Stefanucci and R. van Leeuwen, *Nonequilibrium Many-Body Theory of Quantum Systems* (Cambridge University Press, Cambridge, 2013).
[43] R. Ochs, D. Secker, M. Elbing, M. Mayor, and H. B. Weber, Faraday Discuss. **131**, 281 (2006).
[44] D. Q. Andrews, R. P. van Duyne, and M. A. Ratner, Nano Lett. **8**, 1120 (2008).
[45] D. Menashe and B. Laikhtman, Phys. Rev. B **62**, 13430 (2000).
[46] I. Y. Lee, X. Liu, B. Kosko, and C. Zhou, Nano Lett. **3**, 1683 (2003).
[47] I. Lee, X. Liu, C. Zhou, and B. Kosko, IEEE Trans. Nano. **5**, 613 (2005).
[48] F. Hartmann, D. Hartmann, P. Kowalzik, A. Forchel, L. Gammaitoni, and L. Worschech, Appl. Phys. Lett. **96**, 172110 (2010).
[49] F. Hartmann, D. Hartmann, P. Kowalzik, L. Gammaitoni, A. Forchel, and L. Worschech, Appl. Phys. Lett. **96**, 082108 (2010).
[50] O. V. Konstantinov and V. I. Perel', Zh. Eksp. Teor. Fiz. **39**, 197 (1961) [Sov. Phys.–JETP **12**, 142 (1961)].

[51] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics: Green's Function Methods in Equilibrium and Nonequilibrium Problems* (Benjamin, New York, 1962).
[52] L. V. Keldysh, Zh. Eksp. Teor. Fiz. **47**, 1515 (1964) [Sov. Phys.–JETP **20**, 4 (1964)].
[53] P. Danielewicz, Ann. Phys. (NY) **152**, 239 (1984).
[54] M. Ridley, A. MacKinnon, and L. Kantorovich, Phys. Rev. B **91**, 125433 (2015).
[55] M. Ridley, A. MacKinnon, and L. Kantorovich, J. Phys.: Conf. Ser. **696**, 012017 (2016).
[56] G. Stefanucci and C.-O. Almbladh, Phys. Rev. B **69**, 195318 (2004).
[57] R. Tuovinen, R. van Leeuwen, E. Perfetto, and G. Stefanucci, J. Phys.: Conf. Ser. **427**, 012014 (2013).
[58] A.-P. Jauho, N. S. Wingreen, and Y. Meir, Phys. Rev. B **50**, 5528 (1994).
[59] V. A. Sydoruk, D. Xiang, S. A. Vitusevich, M. V. Petrychuk, A. Vladyka, Y. Zhang, A. Offenhäusser, V. A. Kochelap, A. E. Belyaev, and D. Mayer, J. Appl. Phys. **112**, 014908 (2012).
[60] R. Tuovinen, E. Perfetto, G. Stefanucci, and R. van Leeuwen, Phys. Rev. B **89**, 085131 (2014).
[61] C. A. Perroni, A. Nocera, and V. Cataudella, Europhys. Lett. **103**, 58001 (2013).
[62] V. Vovchenko, D. Anchishkin, J. Azema, P. Lombardo, R. Hayn, and A.-M. Daré, J. Phys.: Condens. Matter **26**, 015306 (2014).
[63] D. C. Langreth, *Linear and Non-Linear Response Theory with Applications*, Vol. 17 of NATO Advanced Studies Series B (Plenum, New York, 1976), p. 3.
[64] H. Mori, Prog. Theor. Phys. **33**, 423 (1965).
[65] H. Risken, *The Fokker-Planck Equation: Methods of Solutions and Applications*, 3rd ed. (Springer, Berlin, 2011).
[66] H. Sumi, J. Chem. Phys. **67**, 2943 (1977).
[67] A. Blumen and R. Silbey, J. Chem. Phys. **69**, 3589 (1978).
[68] I. Rips, Phys. Rev. E **47**, 67 (1993).
[69] R. Bartussek, P. Reimann, and P. Hänggi, Phys. Rev. Lett. **76**, 1166 (1996).
[70] X. Chen, J. Cao, and R. J. Silbey, J. Chem. Phys. **138**, 224104 (2013).
[71] W. J. Thompson, Comput. Phys. **7**, 627 (1993).
[72] H. O. Di Rocco and M. Aguirre Téllez, Acta Phys. Pol., A **106**, 817 (2004).
[73] M. Büttiker, Phys. Rev. B **33**, 3020 (1986).
[74] B. Wang, J. Li, F. Xu, Y. Wei, J. Wang, and H. Guo, Nanoscale **7**, 10030 (2015).
[75] T. Ozaki, Phys. Rev. B **75**, 035123 (2007).
[76] A. Croy and U. Saalmann, Phys. Rev. B **80**, 073102 (2009).
[77] J. Hu, R. Xu, and Y. Yan, J. Chem. Phys. **133**, 101106 (2010).
[78] J. Hu, M. Luo, F. Jiang, R. Xu, and Y. Yan, J. Chem. Phys. **134**, 244106 (2011).
[79] Y. Zhang, C. Y. Yam, and G. Chen, J. Chem. Phys. **138**, 164121 (2013).
[80] H. Xie, Y. Kwok, Y. Zhang, F. Jiang, Y. Yan, and G. Chen, Phys. Status Solidi **250**, 2481 (2013).
[81] P. Reimann, M. Grifoni, and P. Hänggi, Phys. Rev. Lett. **79**, 10 (1997).
[82] S. Kohler, J. Lehmann, and P. Hänggi, Phys. Rep. **406**, 379 (2005).
[83] S. Denisov, L. Morales-Molina, S. Flach, and P. Hänggi, Phys. Rev. A **75**, 063424 (2007).
[84] M. Strass, P. Hänggi, and S. Kohler, Phys. Rev. Lett. **95**, 130601 (2005).
[85] V. Mujica, M. Kemp, and M. A. Ratner, J. Chem. Phys. **101**, 6849 (1994).
[86] V. Mujica, M. Kemp, and M. A. Ratner, J. Chem. Phys. **101**, 6856 (1994).
[87] J. Lehmann, S. Kohler, P. Hänggi, and A. Nitzan, Phys. Rev. Lett. **88**, 228305 (2002).
[88] S. Chen, H. Xie, Y. Zhang, X. Cui, and G. Chen, Nanoscale **5**, 169 (2013).
[89] G. Rubio-Bollinger, C. de las Heras, E. Bascones, N. Agraït, F. Guinea, and S. Vieira, Phys. Rev. B **67**, 121407(R) (2003).
[90] M. F. Goffman, R. Cron, A. Levy Yeyati, P. Joyez, M. H. Devoret, D. Esteve, and C. Urbina, Phys. Rev. Lett. **85**, 170 (2000).
[91] S. Tsukamoto and K. Hirose, Phys. Rev. B **66**, 161402 (2002).
[92] X. Xiao, B. Xu, and N. J. Tao, Nano Lett. **4**, 267 (2004).
[93] A. R. Champagne, A. N. Pasupathy, and D. C. Ralph, Nano Lett. **5**, 305 (2005).
[94] H. Mehrez, A. Wlasenko, B. Larade, J. Taylor, P. Grütter, and H. Guo, Phys. Rev. B **65**, 195419 (2002).
[95] M. D. McDonnell and D. Abbott, PLoS Comput. Biol. **5**. 1000348 (2009).
[96] L. Cao and D.-j. Wu, Phys. Rev. E **62**, 7478 (2000).
[97] C. A. Perroni, F. Romeo, A. Nocera, V. M. Ramaglia, R. Citro, and V. Cataudella, J. Phys.: Condens. Matter **26**, 365301 (2014).
[98] M. Lerch, Acta Math. **11**, 19 (1887).